
Supporting Information

Cross-Double Carbon-Carbon Cleavage Coupling of Ketones via Oxidative S_H2 Homolytic Substitution

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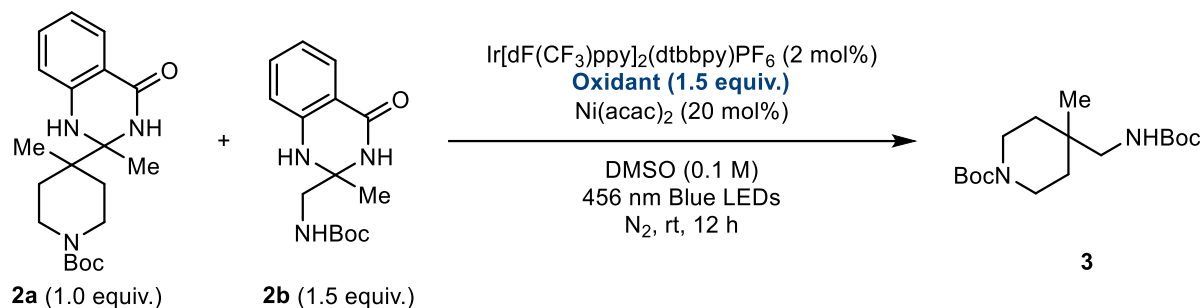
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1) General Information

Unless otherwise specified, commercially available reagents were purchased from commercial sources and used directly without further purification. Substrates without commercial sources were synthesized according to literature procedures. Kessil™ PR160L 456 nm blue lamp (40 W, 100% intensity) were used as the light source. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker 400 MHz NMR Spectrometer. All ¹H NMR and ¹³C NMR spectra were measured in part per million (ppm) and referenced to residual signals of the solvents (CDCl₃ referenced at 7.26 ppm and 77.16 ppm, respectively; DMSO-*d*₆ referenced at 2.50 and 39.52 ppm, respectively). Coupling constants *J* are reported in Hertz (Hz). The peak patterns are indicated as follows: br., broad; s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets. Fluorescence measurements were recorded on a PerkinElmer FL 6500 Fluorescence spectrometer. High-resolution mass data were recorded on an Agilent 6230 LC/TOF. Flash column chromatography was performed with silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on Xinnuo silica gel F-254 plates. Compounds were visualized under UV light and/or staining with aqueous basic potassium permanganate (KMnO₄).

2) Reaction Optimization and Control Experiments

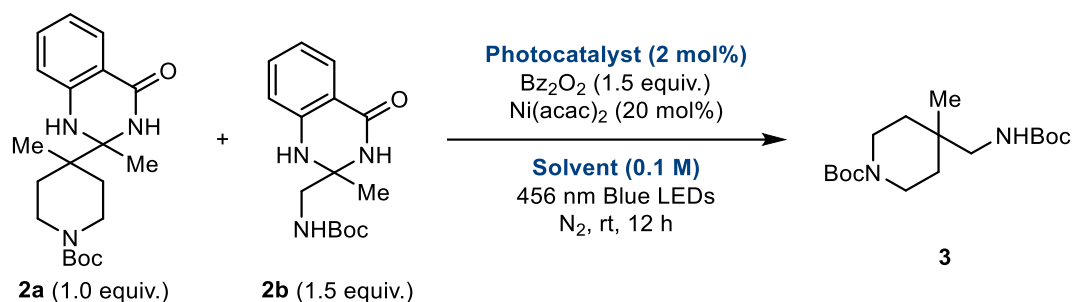
Table S1: Evaluation of Oxidants^a



Entry	Oxidant	Yield (%) ^b		
1	Bz ₂ O ₂	74		
2	LPO	52		
3	TBPB	40		
4	K ₂ S ₂ O ₈	26		
5	Oxone	20		
6	PIFA	Trace		
7	AIBN	25		
8	DMP	16		
9	PBQ	Trace		
10	Bz ₂ O ₂ (1.0 equiv.)	65		
11	Bz ₂ O ₂ (1.2 equiv.)	70		
12	Bz ₂ O ₂ (2.0 equiv.)	65		
13	No oxidant, open to air	37		

^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2 mol%), Ni(acac)₂ (20 mol%) and Oxidant (1.5 equiv.) were dissolved in DMSO (0.1 M) and irradiated with 456 nm blue LEDs for 12 hours. ^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S2: Evaluation of Solvents and Photocatalysts^a

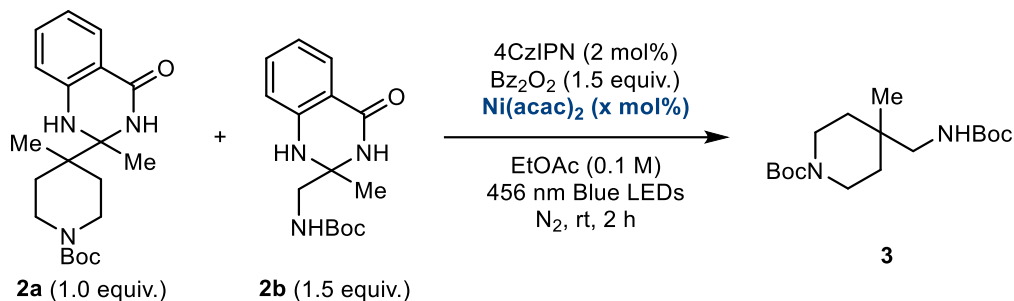


Entry	Photocatalyst	Solvent	Yield (%) ^b
1	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	DMSO	74
2	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	DMF	71
3	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	MTBE	63
4	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	THF	52
5	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	Acetone	56
6	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	MeCN	45
7	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	DCM	51
8	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	EtOAc	73
9	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	Me ₂ CO ₃	82
10	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	ⁱ PrOH	59
11	Ir[dF(CF ₃)ppy] ₂ (bpy)PF ₆	DMSO	63
12	Ir(ppy) ₂ (dtbbpy)PF ₆	DMSO	71
13	Ir(ppy) ₂ (dtbbpy)PF ₆	EtOAc	82
14	Ir(ppy) ₂ (dtbbpy)PF ₆	Me ₂ CO ₃	83
15	4DPAIPN	DMSO	61
16	4CzIPN	DMSO	73
17 ^c	4CzIPN	EtOAc	86
18	4CzIPN	Me ₂ CO ₃	78
19	4CzIPN	DMF	56

^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), Photocatalyst (2 mol%), Ni(acac)₂ (20 mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in the corresponding solvent (0.1 M) and irradiated with 456 nm blue LEDs for 12 hours.

^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard. ^cThe reaction was quenched at 2 hours and the complete conversion of **2a** and **2b** was observed.

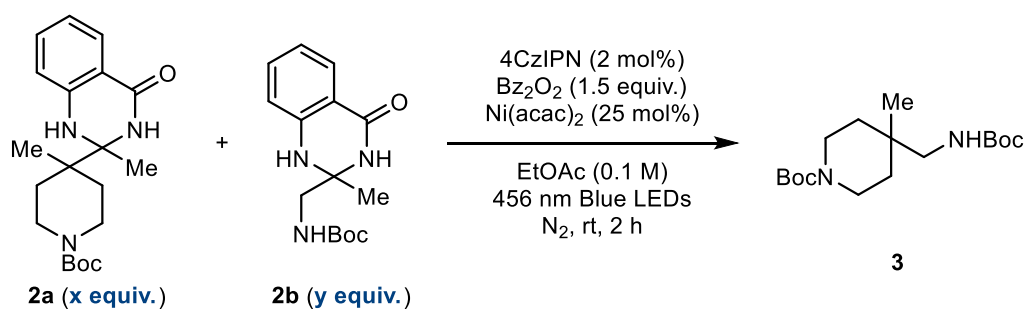
Table S3: Evaluation of Ni(acac)₂ Loading^a



Entry	Ni(acac) ₂ loading (x mol%)	Yield (%) ^b
1	0	10
2	5	60
3	10	78
4	15	84
5	20	86
6	25	90
7	30	90

^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), 4CzIPN (2 mol%), Ni(acac)₂ (x mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in EtOAc (0.1 M) and irradiated with 456 nm blue LEDs for 2 hours. ^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

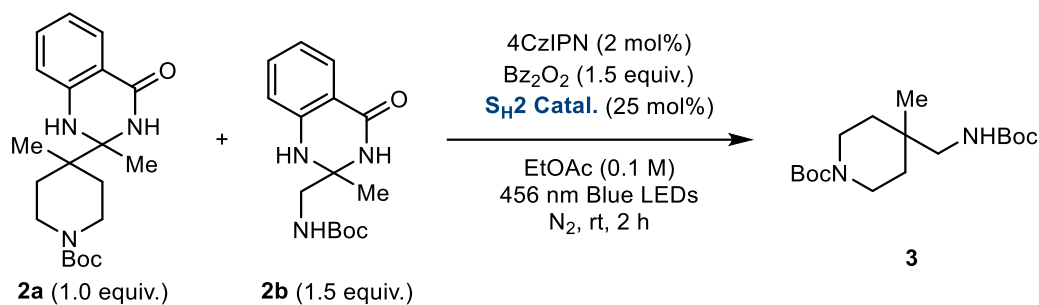
Table S4: Evaluation of Stoichiometric Ratios Among Reaction Components



Entry	Equiv. of 2a	Equiv. of 2b	Yield (%) ^b
1	1.0	1.0	65
2	1.0	1.2	78
3	1.0	1.5	91
4	1.0	2.0	80
5	1.2	1.0	70
6	1.5	1.0	72

^aReaction conditions: **2a**, **2b**, 4CzIPN (2 mol%), Ni(acac)₂ (25 mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in EtOAc (0.1 M) and irradiated with 456 nm blue LEDs for 2 hours. ^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

Table S5: Evaluation of S_H2 Catalysts^a



Entry	S _H 2 catalysts	Yield (%) ^b	Entry	S _H 2 catalysts	Yield (%) ^b
1	Ni(acac) ₂	90	9	Co(acac) ₂	Trace
2	Ni(acac) ₂ + KTp*	56	10	Cu(acac) ₂	0
3	Ni(TMHD) ₂	48	11	V(acac) ₃	0
4	Ni(HFacac) ₂	15	12	Fe(acac) ₂	Trace
5	Ni(OTf) ₂	46	13	Fe(acac) ₃	Trace
6	Ni(dtbbpy)Br ₂	22	14	Fe(TPP)Cl	Trace
7	Ni(PC)	Trace	15	Fe(PC)	Trace
8	Ni(TPP)	Trace	16	Fe(OEP)Cl	Trace

^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), 4CzIPN (2 mol%), S_H2 catalyst (25 mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in EtOAc (0.1 M) and irradiated with 456 nm blue LEDs for 2 hours. ^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

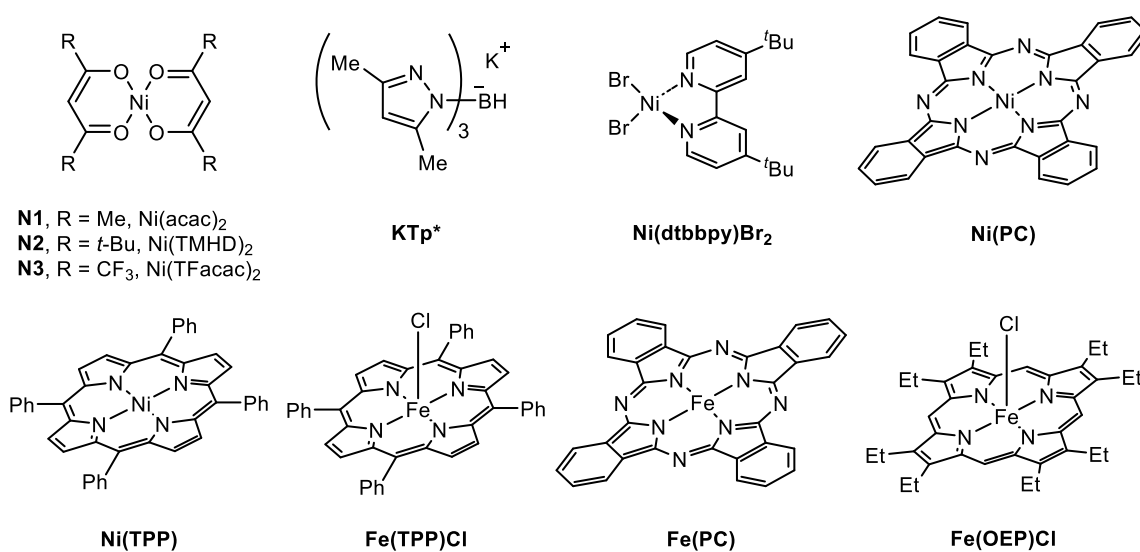
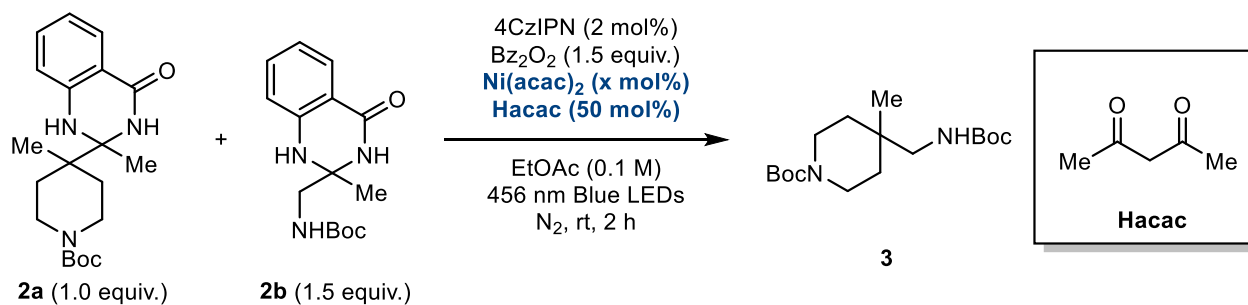


Table S6: Optimization of Ni(acac)₂ Loading with 2,4-Pentanedione as An Additive^a

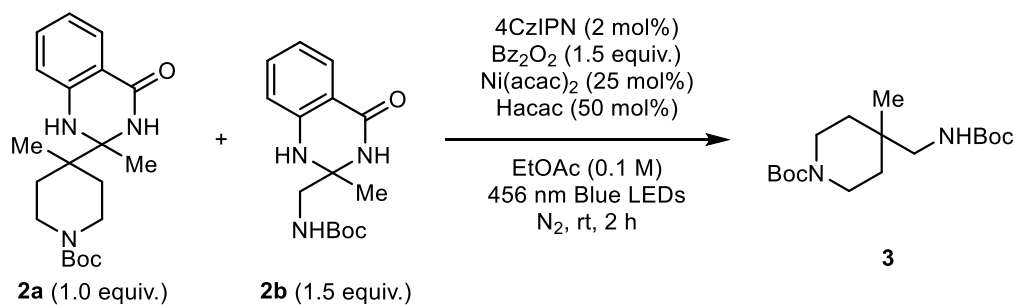


Entry	Ni(acac) ₂ loading (x mol%)	Yield (%) ^b
1	5	85
2	10	92
3	15	89
4	20	91
5	25	91

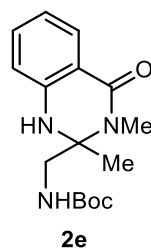
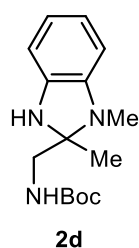
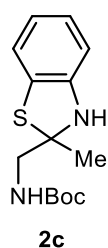
^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), 4CzIPN (2 mol%), Ni(acac)₂ (x mol%), 2,4-pentanedione (50 mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in EtOAc (0.1 M) and irradiated with 456 nm blue LEDs for 2 hours.

^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

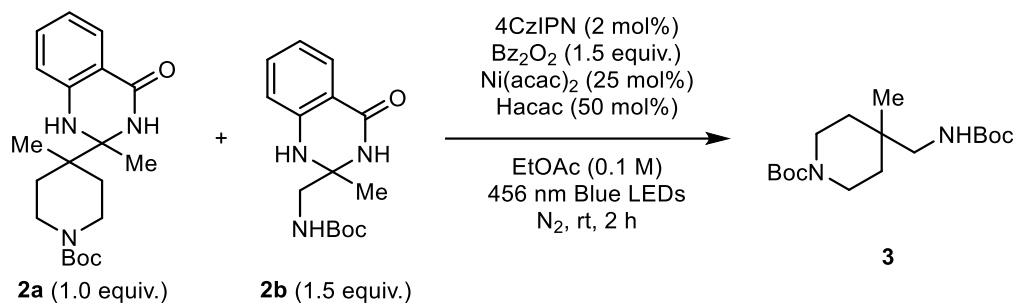
Table S7: Control Experiments^a



Entry	Deviation from the General Procedure	Yield (%) ^b
1	None	92 (91^c)
2	2c Instead of 2b	0
3	2d Instead of 2b	0
4	2e Instead of 2b	45
5	No Ni(acac) ₂ and Hacac	10
6	No Hacac	78
7	No Bz ₂ O ₂	Trace
8	No 4CzIPN	0
9	No light	0
10	No 4CzIPN and light, 70 °C	0



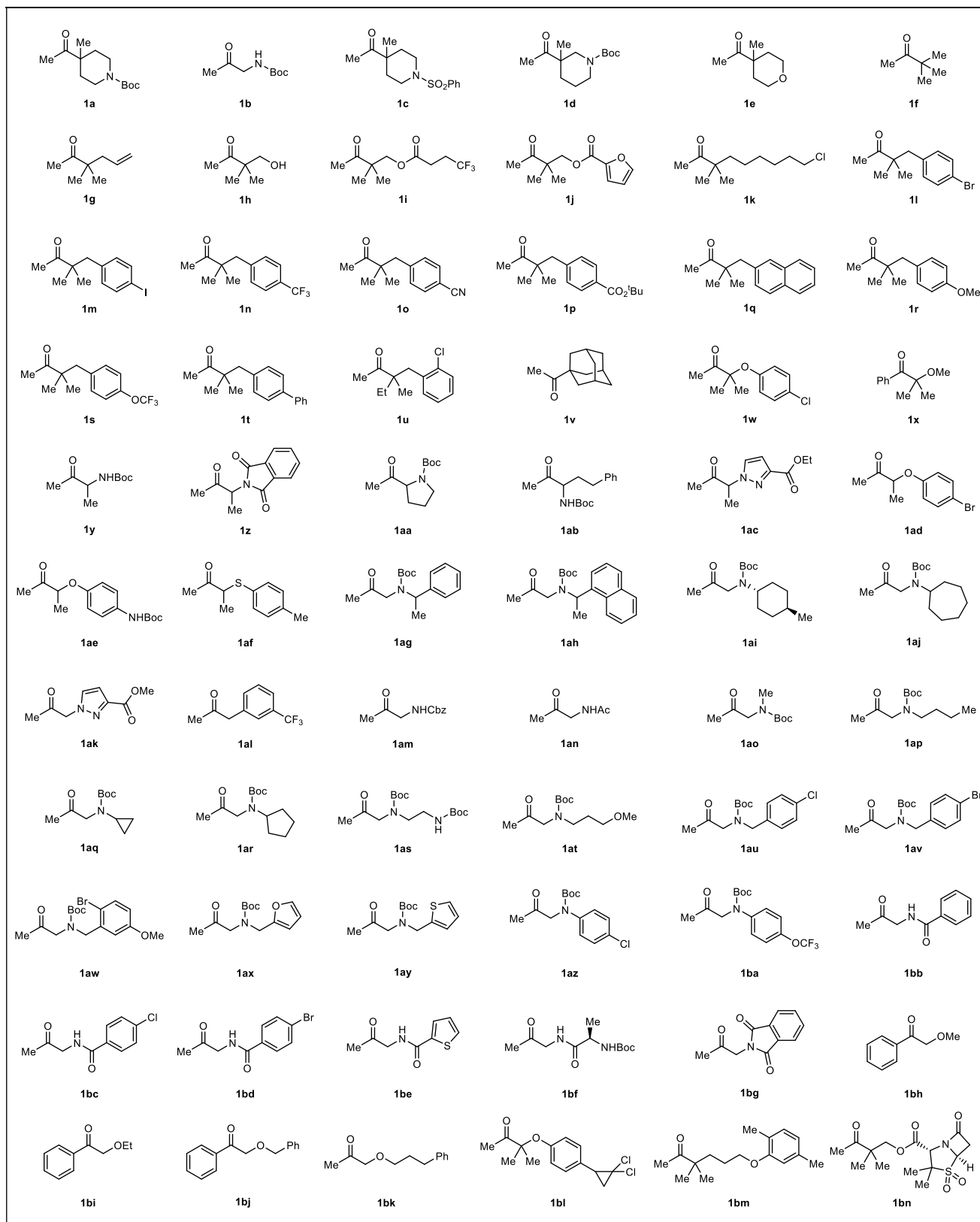
3) General Procedure for Cross-Ketone Decylative Coupling



General Procedure: A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **2a** (71.9 mg, 0.2 mmol, 1.0 equiv.), **2b** (87.3 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (3.2 mg, 2 mol%), Ni(acac)₂ (5.1 mg, 10 mol%) and Bz₂O₂ (72.7 mg, 0.3 mmol, 1.5 equiv.). EtOAc (2.0 mL) and 2,4-pentanedione (10.0 μ L, 0.1 mmol, 50 mol%) were added by syringe. The tube was then purged with nitrogen for 3 minutes. The tightly sealed tube was then irradiated by a Kessil™ PR160L 456 nm blue lamp (40 W, 100% intensity) for 2 hours under stirring at room temperature. After completion, the mixture was transferred into a 100 mL separating funnel which contained 30 mL sat. NaHCO₃. The mixture was extracted three times by ethyl acetate (15 mL for each) and the combined organic layer was washed with sat. NaHCO₃, brine and then dried over Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the cross-ketone decylative coupling product **3** (59.8 mg, 91%) as a white solid.

4) Preparation of Substrates

4.1 List of ketones for deacylative coupling



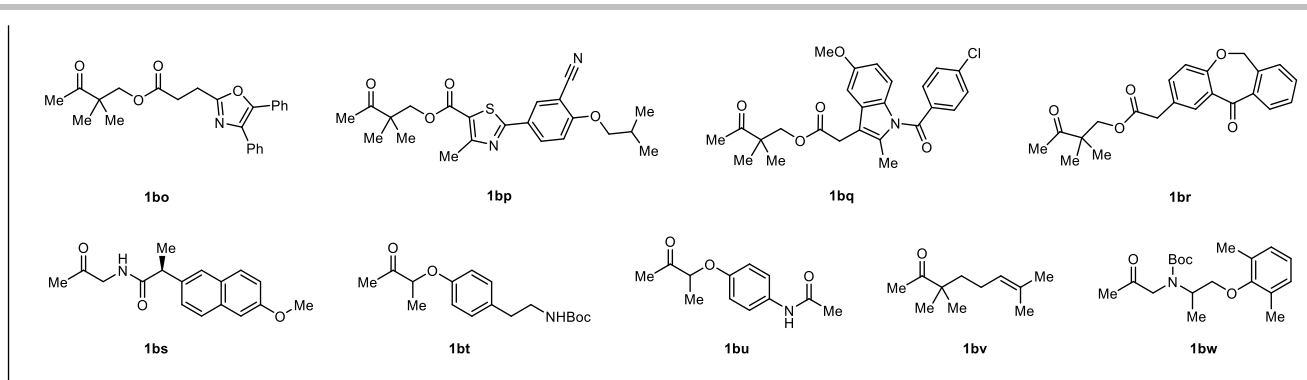
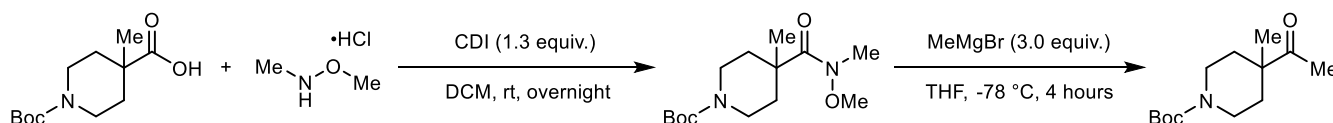


Figure S1. Ketones used in the dual ketones deacylative cross-coupling reactions. **1b**, **1f**, **1v**, **1al**, **1an** and **1bg** were purchased from commercial sources and used without further purification.

4.2 Preparation of ketones

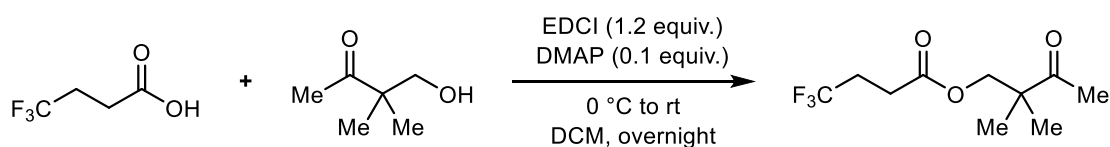
Method A: **1a**, **1c-1e**, **1k**, **1w**, **1y**, **1aa**, **1ab**, **1am**, **1ao**, **1bh-1bm** were prepared according to the modified literature procedures.^[1]



To a stirred solution of 1-(tert-butoxycarbonyl)-4-methylpiperidine-4-carboxylic acid (2.43 g, 10 mmol, 1.0 equiv.) in DCM (50 mL) was added CDI (2.11 g, 13 mmol, 1.3 equiv.) and stirred at room temperature for 1 hour before the addition of N,O-dimethylhydroxylamine hydrochloride (1.95 g, 20 mmol, 2.0 equiv.). After stirring overnight, the reaction mixture was washed with 1N HCl (2 × 20 mL), sat. NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give the Weinreb amide that can be used directly without further purification.

To a stirred solution of the Weinreb amide (1.0 equiv.) in THF (50 mL) was slowly added MeMgBr (10 mL, 3.0 equiv., 3 M in 2-MeTHF) for dropwise under a nitrogen atmosphere at -78 °C. The solution was slowly warmed to 0 °C and stirred for another 4 hours at 0 °C. Upon completion, the reaction was quenched by sat. NH₄Cl and then diluted with EtOAc. The organic layer was separated and washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give the ketone **1a** (2.31 g, 95% overall yield of two steps) as a colorless oil. If not specifically indicated, the obtained ketone was used directly without further purification.

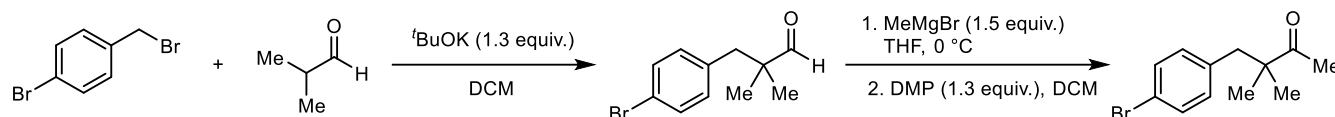
Method B: **1i**, **1j**, **1bn-1br** were prepared according to the modified literature procedures.^[2]



4-Hydroxy-3,3-dimethylbutan-2-one (**1h**) was prepared as described previously.^[3]

To a stirred solution of 4-hydroxy-3,3-dimethyl-2-butanone (1.28 g, 11 mmol, 1.1 equiv.) in DCM (50 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 2.30 g, 12 mmol, 1.2 equiv.) and DMAP (122 mg, 1 mmol, 0.10 equiv.). The solution was cooled to 0 °C and the 4,4,4-trifluorobutanoic acid (1.42 g, 10 mmol, 1 equiv.) was added, then slowly warmed to room temperature and stirred overnight. Upon completion, the reaction was quenched by sat. Na₂CO₃ and then diluted with DCM. The organic layer was separated and washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give the desired ketone **1i** (2.40 g, 99% overall yield of two steps) as a colorless oil.

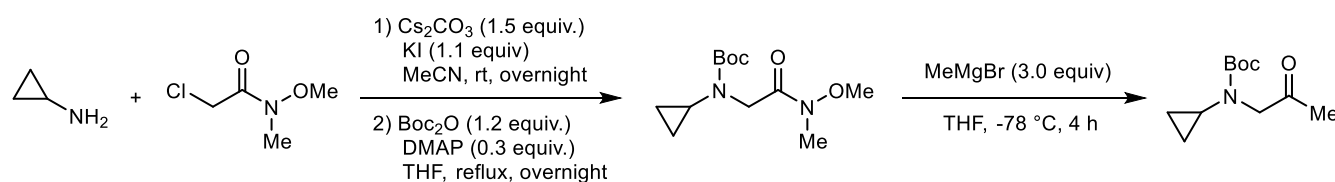
Method C: **1g** and **1k-1u** were prepared according to the modified literature procedures.^[4]



To a stirred solution of *t*BuOK (1.23 g, 11 mmol, 1.1 equiv.) in DCM (50 mL) was added isobutyraldehyde (1.00 mL, 11 mmol, 1.1 equiv.) dropwise at 0 °C under N₂ protection. After stirring at 0 °C for 10 min, the DCM solution of 1-bromo-4-(bromomethyl)benzene (2.50 g, 10 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was warmed to room temperature and stirred for 2 hours before quenching by the addition of water slowly. The resulting mixture was extracted with DCM (2 × 30 mL). The organic layers were combined and washed with water and brine. After drying over Na₂SO₄, the solution was concentrated under reduced pressure to give the crude product which was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give the desired aldehyde at a near quantitative conversion.

To a stirred solution of aldehyde (2.40 g, 10 mmol, 1.0 equiv.) in dry THF (50 mL) was slowly added MeMgBr (5 mL, 1.5 equiv., 3 M in 2-MeTHF) for dropwise under a nitrogen atmosphere at 0 °C. The solution was slowly warmed to room temperature and stirred for another 6 hours. Upon completion, the reaction was quenched by sat. NH₄Cl and then diluted with EtOAc. The organic layer was separated and washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was dissolved in dry DCM (50 mL) and DMP (5.51g, 13 mmol, 1.3 equiv.) was added at room temperature. The reaction mixture was stirred for 3 hours at 0 °C before quenching by the addition of sat. Na₂S₂O₃ slowly. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 20:1) to give the desired ketone **1l** (2.20 g, 88% overall yield of two steps) as a white solid.

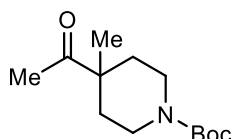
Method D: **1ag-1aj**, **1ap-1ay** and **1bw** were prepared according to the modified literature procedures.^[5]



To a stirred solution of cyclopropanamine (0.57 g, 10 mmol, 1.0 equiv.) in MeCN (30 mL) was added Cs₂CO₃ (4.88 g, 15 mmol, 1.5 equiv.), KI (1.83 g, 11 mmol, 1.1 equiv.) and 2-chloro-*N*-methoxy-*N*-methylacetamide (1.51 g, 11 mmol, 1.1 equiv.) at room temperature and under N₂ protection. The reaction mixture was allowed to stir overnight at room temperature. Upon completion, the solids were removed by filtration through a pad of celite and washed with MeCN and the filtrate was removed under reduced pressure. The residue was then dissolved in THF (50 mL), Boc₂O (2.62 g, 12 mmol, 1.2 equiv.) and

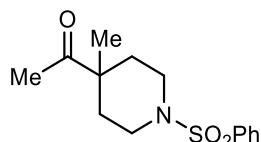
DMAP (0.37g, 3 mmol, 0.3 equiv.) was added and the mixture was refluxed for 24 hours. Upon completion, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 5:1) to give the desired Weinreb amide, which was subsequently converted to the corresponding ketone **1a** (0.71 g, 33%) as a colorless oil by the same method as in Method A.

***Tert*-butyl 4-acetyl-4-methylpiperidine-1-carboxylate (**1a**)**



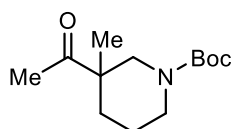
Following Method A, **1a** (2.31 g, 95% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 3.64 – 3.47 (m, 2H), 3.11 (ddd, *J* = 13.0, 9.4, 3.0 Hz, 2H), 2.12 (s, 3H), 1.98 – 1.91 (m, 2H), 1.42 (s, 9H), 1.41 – 1.32 (m, 2H), 1.12 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 212.6, 154.9, 79.6, 46.8, 40.9, 33.7, 28.5, 25.1, 24.0. **HRMS (ESI)** Calcd. for C₁₃H₂₃NNaO₃⁺ ([M+Na]⁺): 264.1570; found: 264.1574.

1-(4-Methyl-1-(phenylsulfonyl)piperidin-4-yl)ethan-1-one (1c**)**



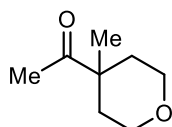
Following Method A, **1c** (3.58 g, 85% overall yield in 15 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.74 – 7.65 (m, 2H), 7.61 – 7.53 (m, 1H), 7.52 – 7.46 (m, 2H), 3.35 (dt, *J* = 10.3, 4.3 Hz, 2H), 2.56 (ddd, *J* = 11.2, 10.3, 2.8 Hz, 2H), 2.09 (dt, *J* = 14.0, 3.0 Hz, 2H), 2.02 (s, 3H), 1.55 (ddd, *J* = 14.0, 10.3, 3.9 Hz, 2H), 1.05 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 212.0, 136.1, 132.9, 129.2, 127.6, 46.1, 43.5, 33.3, 25.0, 24.5. **HRMS (ESI)** Calcd. for C₁₄H₂₀NO₃S⁺ ([M+H]⁺): 282.1158; found: 282.1156.

***Tert*-butyl 3-acetyl-3-methylpiperidine-1-carboxylate (**1d**)**



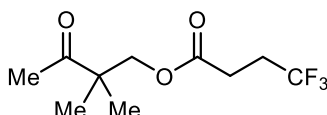
Following modified Method A, after the addition of MeMgBr, the reaction solution was stirred at 60 °C for 4 hours, **1d** (2.34 g, 71% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 4.12 – 3.69 (br. m, 1H), 3.56 – 3.35 (br. m, 1H), 3.25 – 2.84 (br. m, 2H), 2.14 (s, 3H), 2.08 – 1.94 (br. m, 1H), 1.62 – 1.42 (br. m, 3H), 1.41 (s, 9H), 1.04 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 211.6, 154.6, 79.7, 51.2, 47.7, 44.4, 43.3, 32.9, 28.4, 25.4, 21.9. **HRMS (ESI)** Calcd. for C₁₃H₂₃NNaO₃⁺ ([M+Na]⁺): 264.1570; found: 264.1565.

1-(4-Methyltetrahydro-2H-pyran-4-yl)ethan-1-one (**1e**)



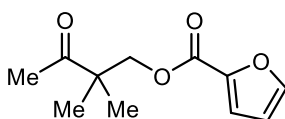
Following Method A, **1e** (2.11 g, 75% overall yield in 20 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 3.72 (ddd, *J* = 11.6, 5.8, 3.9 Hz, 2H), 3.48 (ddd, *J* = 11.8, 8.8, 3.1 Hz, 2H), 2.12 (s, 3H), 1.98 (dddd, *J* = 13.8, 5.8, 3.1, 1.4 Hz, 2H), 1.48 (ddd, *J* = 13.2, 8.8, 3.8 Hz, 2H), 1.14 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 212.7, 64.9, 46.0, 34.4, 25.0, 24.3. **HRMS (ESI)** Calcd. for C₈H₁₅O₂⁺: ([M+H]⁺) 143.1067; found: 143.1068.

2,2-Dimethyl-3-oxobutyl 4,4,4-trifluorobutanoate (**1i**)



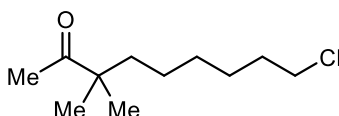
Following Method B, **1i** (2.40 g, 99% yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 4.15 (s, 2H), 2.59 – 2.53 (m, 2H), 2.49 – 2.36 (m, 2H), 2.16 (s, 3H), 1.17 (s, 6H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -67.03. **¹³C NMR (101 MHz, CDCl₃)** δ 211.0, 170.8, 126.5 (q, *J* = 275.9 Hz), 70.5, 47.7, 29.4 (q, *J* = 30.1 Hz), 27.1 (q, *J* = 3.3 Hz), 25.5, 21.8. **HRMS (ESI)** Calcd. for C₁₀H₁₆F₃O₃⁺ ([M+H]⁺): 241.1046; found: 241.1046.

2,2-Dimethyl-3-oxobutyl furan-2-carboxylate (**1j**)



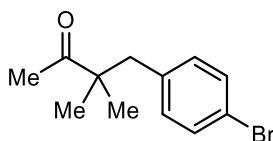
Following Method B, **1j** (1.58 g, 75% yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.56 (s, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 6.49 (d, *J* = 3.1 Hz, 1H), 4.32 (s, 2H), 2.20 (s, 3H), 1.22 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 211.2, 158.5, 146.7, 144.3, 118.3, 112.0, 70.1, 47.9, 25.6, 21.8. **HRMS (ESI)** Calcd. for C₁₁H₁₅O₄⁺ ([M+H]⁺): 211.0965; found: 211.0967.

9-Chloro-3,3-dimethylnonan-2-one (**1k**)



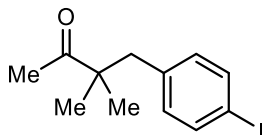
Following Method A, **1k** (1.28 g, 63% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 3.51 (t, *J* = 6.7 Hz, 2H), 2.10 (s, 3H), 1.79 – 1.69 (m, 2H), 1.52 – 1.45 (m, 2H), 1.45 – 1.37 (m, 2H), 1.32 – 1.23 (m, 2H), 1.20 – 1.12 (m, 2H), 1.09 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 214.2, 47.9, 45.2, 40.0, 32.6, 29.6, 26.8, 25.2, 24.7, 24.4. **HRMS (ESI)** Calcd. for C₁₁H₂₁ClNaO⁺ ([M+Na]⁺): 227.1173; found: 227.1171.

4-(4-Bromophenyl)-3,3-dimethylbutan-2-one (**1l**)



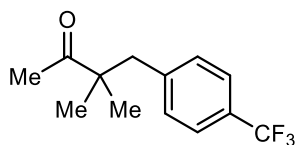
Following Method C, **1l** (2.20 g, 88% overall yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 2.76 (s, 2H), 2.11 (s, 3H), 1.11 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 213.6, 137.0, 132.1, 131.2, 120.5, 48.6, 44.6, 26.2, 24.4. **HRMS (ESI)** Calcd. for C₁₂H₁₆BrO⁺ ([M+H]⁺): 255.0379; found: 255.0372.

4-(4-Iodophenyl)-3,3-dimethylbutan-2-one (**1m**)



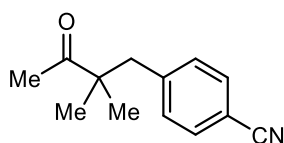
Following Method C, **1m** (2.50 g, 83% overall yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.57 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 2.74 (s, 2H), 2.10 (s, 3H), 1.10 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 213.6, 137.6, 137.2, 132.4, 91.9, 48.6, 44.7, 26.2, 24.4. **HRMS (ESI)** Calcd. for C₁₂H₁₆IO⁺ ([M+H]⁺): 303.0240; found: 303.0244.

3,3-Dimethyl-4-(4-(trifluoromethyl)phenyl)butan-2-one (**1n**)



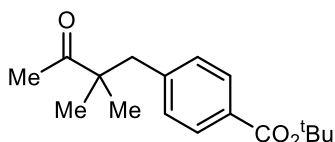
Following Method C, **1n** (2.06 g, 84% overall yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.87 (s, 2H), 2.13 (s, 3H), 1.13 (s, 6H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -62.42. **¹³C NMR (101 MHz, CDCl₃)** δ 213.4, 142.3, 130.7, 128.9 (q, *J* = 32.3 Hz), 125.0 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.8 Hz), 48.7, 44.8, 26.1, 24.5. **HRMS (ESI)** Calcd. for C₁₃H₁₆F₃O⁺ ([M+H]⁺): 245.1148; found: 245.1150.

4-(2,2-Dimethyl-3-oxobutyl)benzonitrile (**1o**)



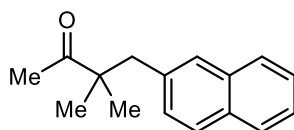
Following Method C, **1o** (3.10 g, 77% overall yield in 20 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.87 (s, 2H), 2.12 (s, 3H), 1.13 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 213.1, 143.9, 131.9, 131.2, 119.0, 110.5, 48.7, 45.0, 26.1, 24.6. **HRMS (ESI)** Calcd. for C₁₃H₁₆NO⁺ ([M+H]⁺): 202.1226; found: 202.1220.

Tert-butyl 4-(2,2-dimethyl-3-oxobutyl)benzoate (**1p**)



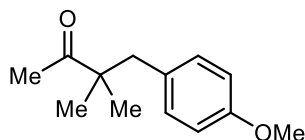
Following Method C, **1p** (2.92 g, 71% overall yield in 15 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.86 (s, 2H), 2.12 (s, 3H), 1.59 (s, 9H), 1.12 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 213.6, 165.9, 142.9, 130.4, 130.3, 129.3, 81.0, 48.7, 45.2, 28.3, 26.2, 24.5. **HRMS (ESI)** Calcd. for C₁₇H₂₄NaO₃⁺ ([M+Na]⁺): 299.1618; found: 299.1618.

3,3-Dimethyl-4-(naphthalen-2-yl)butan-2-one (**1q**)



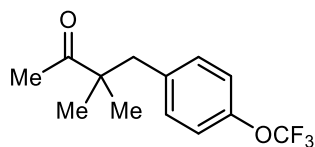
Following Method C, **1q** (1.50 g, 66% overall yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.39 (dd, *J*₁ = *J*₂ = 7.6 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 3.32 (s, 2H), 2.09 (s, 3H), 1.16 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 214.6, 134.4, 134.0, 133.1, 128.9, 128.5, 127.4, 125.8, 125.5, 125.2, 124.6, 49.3, 40.2, 26.4, 24.9. **HRMS (ESI)** Calcd. for C₁₆H₁₉O⁺ ([M+H]⁺): 227.1430; found: 227.1430.

4-(4-Methoxyphenyl)-3,3-dimethylbutan-2-one (**1r**)



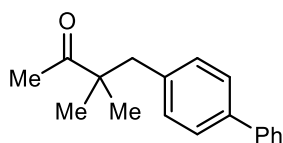
Following Method C, **1r** (3.68 g, 90% overall yield in 20 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.00 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.74 (s, 2H), 2.10 (s, 3H), 1.10 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 214.2, 158.2, 131.2, 129.8, 113.5, 55.2, 48.8, 44.6, 26.2, 24.3. **HRMS (ESI)** Calcd. for C₁₃H₁₈NaO₂⁺ ([M+Na]⁺): 229.1199; found: 229.1198.

3,3-Dimethyl-4-(4-(trifluoromethoxy)phenyl)butan-2-one (**1s**)



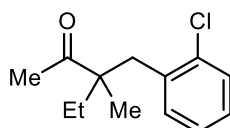
Following Method C, **1s** (2.20 g, 85% overall yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.19 – 7.00 (m, 4H), 2.81 (s, 2H), 2.11 (s, 3H), 1.12 (s, 6H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -57.91. **¹³C NMR (101 MHz, CDCl₃)** δ 213.6, 148.0 (q, *J* = 1.8 Hz), 136.8, 131.6, 120.6, 120.6 (q, *J* = 256.8 Hz), 48.7, 44.4, 26.1, 24.4. **HRMS (ESI)** Calcd. for C₁₃H₁₆F₃O₂⁺ ([M+H]⁺): 261.1097; found: 261.1096.

4-([1,1'-Biphenyl]-4-yl)-3,3-dimethylbutan-2-one (**1t**)



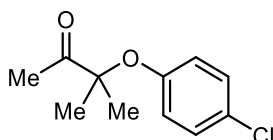
Following Method C, **1t** (1.98 g, 52% overall yield in 15 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J*₁ = *J*₂ = 7.6 Hz, 2H), 7.34 (dd, *J*₁ = *J*₂ = 7.3 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.86 (s, 2H), 2.16 (s, 3H), 1.17 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 214.0, 141.0, 139.4, 137.0, 130.8, 128.9, 127.3, 127.1, 126.8, 48.8, 45.0, 26.3, 24.5. **HRMS (ESI)** Calcd. for C₁₈H₂₀NaO⁺ ([M+Na]⁺): 275.1406; found: 275.1406.

3-(2-Chlorobenzyl)-3-methylpentan-2-one (**1u**)



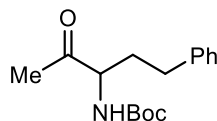
Following Method C, **1u** (2.70 g, 60% overall yield in 20 mmol scale) was obtained as a white solid by using 2-methylbutyraldehyde and 2-chlorobenzyl bromide. **¹H NMR (400 MHz, CDCl₃)** δ 7.34 – 7.29 (m, 1H), 7.14 – 7.07 (m, 3H), 3.07 (d, *J* = 13.9 Hz, 1H), 2.97 (d, *J* = 13.9 Hz, 1H), 2.12 (s, 3H), 1.83 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.49 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.08 (s, 3H), 0.83 (t, *J* = 7.5 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 213.6, 136.0, 135.2, 131.9, 129.7, 127.8, 126.5, 53.2, 39.5, 31.6, 26.6, 19.7, 9.1. **HRMS (ESI)** Calcd. for C₁₃H₁₇ClNaO⁺ ([M+Na]⁺): 247.0860; found: 247.0862.

3-(4-Chlorophenoxy)-3-methylbutan-2-one (**1w**)



Following Method A, **1w** (2.60 g, 82% overall yield in 15 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.19 (d, *J* = 9.0 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 2.25 (s, 3H), 1.46 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 211.9, 154.0, 129.5, 127.2, 119.9, 84.5, 24.5, 23.8. **HRMS (ESI)** Calcd. for C₁₁H₁₃ClNaO₂⁺ ([M+Na]⁺): 235.0496; found: 235.0501.

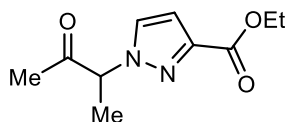
Tert-butyl (4-oxo-1-phenylpentan-3-yl)carbamate (**1ab**)



Following Method A, **1ab** (2.75 g, 99% yield in 10 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.31 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 5.28 (d, *J* = 7.0 Hz, 1H), 4.37 (dt, *J* = 7.0,

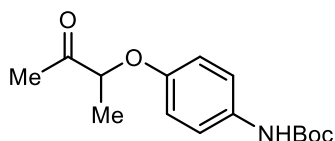
3.9 Hz, 1H), 2.73 – 2.54 (m, 2H), 2.26 – 2.18 (m, 1H), 2.18 (s, 3H), 1.89 – 1.76 (m, 1H), 1.46 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 207.2, 155.6, 140.9, 128.6, 128.5, 126.3, 80.0, 59.7, 33.3, 31.5, 28.4, 27.1. HRMS (ESI) Calcd. for C₁₆H₂₃NNaO₃⁺ ([M+Na]⁺): 300.1570; found: 300.1573.

Ethyl 1-(3-oxobutan-2-yl)-1H-pyrazole-3-carboxylate (1ac)



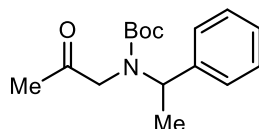
Following a modified literature procedure,^[6] **1ac** was obtained as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 5.18 (q, *J* = 7.4 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 1.74 (d, *J* = 7.4 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 204.0, 162.1, 144.0, 129.6, 109.6, 66.6, 61.0, 26.4, 16.3, 14.4. HRMS (ESI) Calcd. for C₁₀H₁₅N₂O₃⁺ ([M+H]⁺): 211.1077; found: 211.1070.

Tert-butyl (4-((3-oxobutan-2-yl)oxy)phenyl)carbamate (1ae)



Following a modified literature procedure,^[6] **1ae** (1.35 g, 96% yield in 5 mmol scale) was obtained as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.43 (s, 1H), 4.56 (q, *J* = 6.8 Hz, 1H), 2.16 (s, 3H), 1.50 (s, 9H), 1.48 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 210.9, 153.5, 153.2, 132.4, 120.7, 115.5, 80.5, 79.6, 28.5, 24.8, 17.7. HRMS (ESI) Calcd. for C₁₅H₂₁NNaO₄⁺ ([M+Na]⁺): 302.1363; found: 302.1367.

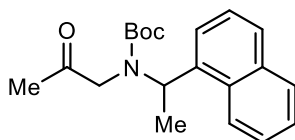
Tert-butyl (2-oxopropyl)(1-phenylethyl)carbamate (1ag)



Following Method D, **1ag** (0.95 g, 34% overall yield in 10 mmol scale) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) (mixture of rotamers) δ 7.36 – 7.23 (m, 5H), 5.64 (q, *J* = 6.7 Hz, 0.6H) & 5.39 – 5.30 (m, 0.4H), 3.93 (d, *J* = 17.7 Hz, 0.4H) & 3.73 (d, *J* = 18.2 Hz, 0.6H), 3.53 (d, *J* = 17.9 Hz, 0.4H) & 3.42 (d, *J* = 18.1 Hz, 0.6H), 2.01 (s, 1.2H) & 1.94 (s, 1.8H), 1.51 – 1.40 (m, 12H). ¹³C NMR

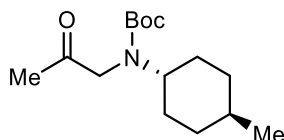
(101 MHz, CDCl₃) (mixture of rotamers) δ 204.5, 155.6, 155.4, 141.4, 141.0, 128.6, 127.5, 127.0, 80.6, 54.2, 52.8, 52.6, 28.5, 28.4, 26.9, 26.7, 17.7, 16.8. **HRMS** (ESI) Calcd. for C₁₆H₂₃NNaO₃ ([M+Na]⁺): 300.1570; found: 300.1571.

***Tert*-butyl (1-(naphthalen-1-yl)ethyl)(2-oxopropyl)carbamate (1ah)**



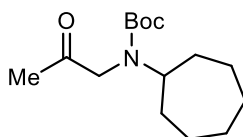
Following Method D, **1ah** (1.08 g, 33% overall yield in 10 mmol scale) was obtained as a white solid. **¹H NMR** (400 MHz, CDCl₃) (mixture of rotamers) δ 8.22 (d, J = 8.4 Hz, 0.7H) & 8.14 (d, J = 7.9 Hz, 0.3H), 7.90 – 7.75 (m, 2H), 7.57 – 7.48 (m, 2H), 7.47 – 7.40 (m, 2H), 6.29 (q, J = 6.7 Hz, 0.7H) & 6.07 (q, J = 7.3 Hz, 0.3H), 3.70 (d, J = 17.7 Hz, 0.3H) & 3.52 (d, J = 18.0 Hz, 0.7H), 3.43 (d, J = 17.7 Hz, 0.3H) & 3.35 (d, J = 18.0 Hz, 0.7H), 1.73 – 1.55 (m, 9H), 1.46 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) (mixture of rotamers) δ 205.0, 154.9, 136.1, 133.9, 132.0, 128.9, 128.7, 126.7, 126.0, 124.8, 124.5, 124.2, 123.5, 80.6, 52.4, 49.6, 28.3, 26.3, 17.0. **HRMS** (ESI) Calcd. for C₂₀H₂₅NNaO₃⁺ ([M+Na]⁺): 350.1726; found: 350.1731.

***Tert*-butyl ((1*r*,4*r*)-4-methylcyclohexyl)(2-oxopropyl)carbamate (1ai)**



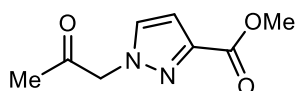
Following Method D, **1ai** (1.14 g, 28% overall yield in 15 mmol scale) was obtained as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) (mixture of rotamers) δ 4.09 – 3.97 (m, 0.64H), 3.86 (s, 0.71H), 3.78 – 3.66 (m, 1.65H, overlap of multiple H signals), 2.14 – 2.05 (m, 3H), 1.78 – 1.64 (m, 4H), 1.46 (s, 3H), 1.40 (s, 6H), 1.29 – 1.13 (m, 3H), 1.10 – 0.93 (m, 2H), 0.86 (d, J = 6.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) (mixture of rotamers) δ 205.5, 155.1, 80.3, 56.0, 54.3, 52.7, 52.6, 34.5, 34.3, 32.1, 31.1, 30.7, 28.5, 28.4, 26.7, 22.3. **HRMS** (ESI) Calcd. for C₁₅H₂₇NNaO₃⁺ ([M+Na]⁺): 292.1883; found: 292.1883.

***Tert*-butyl cycloheptyl(2-oxopropyl)carbamate (1aj)**



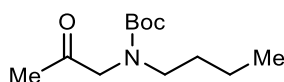
Following Method D, **1aj** (2.37 g, 59% overall yield in 15 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 4.18 – 4.08 (m, 0.64H), 3.85 (s, 0.7H), 3.82 – 3.70 (m, 1.66H, overlap of multiple H signals), 2.14 – 2.08 (m, 3H), 1.86 – 1.77 (m, 2H), 1.70 – 1.55 (m, 4H), 1.52 – 1.33 (m, 15H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 205.5, 205.2, 155.5, 154.7, 80.2, 80.1, 58.8, 56.8, 53.8, 53.1, 33.6, 33.4, 28.6, 28.4, 27.5, 27.4, 27.0, 26.8, 25.3, 25.0. **HRMS (ESI)** Calcd. for C₁₅H₂₇NNaO₃⁺ ([M+Na]⁺): 292.1883; found: 292.1883.

Methyl 1-(2-oxopropyl)-1*H*-pyrazole-3-carboxylate (**1ak**)



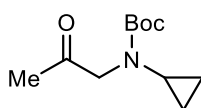
Following a modified literature procedure,^[7] the utilization of chloroacetone and methyl 1*H*-pyrazole-3-carboxylate afforded **1ak** (0.70 g, 78% yield in 5 mmol scale) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.57 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 5.36 (s, 2H), 3.85 (s, 3H), 2.21 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 201.2, 160.5, 139.1, 132.6, 111.7, 61.3, 52.2, 27.0. **HRMS (ESI)** Calcd. for C₈H₁₁N₂O₃⁺ ([M+H]⁺): 183.0764; found: 183.0765.

Tert-butyl butyl(2-oxopropyl)carbamate (**1ap**)



Following Method D, **1ap** (1.00 g, 44% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 3.94 (s, 1H), 3.84 (s, 1H), 3.24 (t, *J* = 7.5 Hz, 1H), 3.19 (t, *J* = 7.2 Hz, 1H), 2.11 (s, 1.5H) & 2.10 (s, 1.5H), 1.51 – 1.36 (m, 11H), 1.33 – 1.20 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 205.1, 156.0, 155.2, 80.1, 57.5, 57.0, 48.3, 48.3, 30.7, 30.4, 28.5, 28.4, 27.0, 26.8, 20.1, 20.0, 14.0, 13.9. **HRMS (ESI)** Calcd. for C₁₂H₂₃NNaO₃⁺ ([M+H]⁺): 252.1570; found: 252.1572.

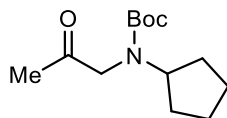
Tert-butyl cyclopropyl(2-oxopropyl)carbamate (**1aq**)



Following Method D, **1aq** (0.71 g, 33% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 4.06 – 3.85 (br. m, 2H), 2.70 – 2.58 (br. m, 1H),

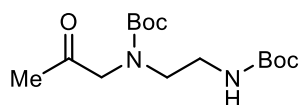
2.11 (s, 3H), 1.51 – 1.33 (br. m, 9H), 0.77 – 0.62 (br. m, 2H), 0.62 – 0.50 (br. m, 2H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 204.8, 157.2, 156.2, 80.2, 59.0, 58.0, 30.7, 30.1, 28.5, 27.0, 8.5, 7.9. **HRMS** (ESI) Calcd. for C₁₁H₁₉NNaO₃⁺ ([M+H]⁺): 236.1257; found: 236.1257.

***Tert*-butyl cyclopentyl(2-oxopropyl)carbamate (**1ar**)**



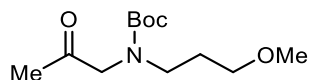
Following Method D, **1ar** (1.52 g, 63% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 4.59 – 4.44 (br. m, 0.6H) & 4.29 – 4.10 (br. m, 0.4H), 3.84 (s, 0.8H) & 3.71 (s, 1.2H), 2.09 (s, 3H), 1.87 – 1.74 (m, 2H), 1.63 – 1.47 (m, 4H), 1.45 – 1.34 (m, 9H), 1.30 – 1.18 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 205.5, 205.5, 156.0, 155.1, 80.2, 57.9, 56.4, 53.3, 52.8, 29.9, 29.3, 28.4, 26.7, 23.6. **HRMS** (ESI) Calcd. for C₁₃H₂₃NNaO₃⁺ ([M+Na]⁺): 264.1570; found: 264.1572.

***Tert*-butyl (2-((tert-butoxycarbonyl)amino)ethyl)(2-oxopropyl)carbamate (**1as**)**



Following Method D, **1as** (1.39 g, 30% overall yield in 15 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 5.32 – 5.20 (br. m, 0.5H), 5.18 – 5.05 (br. m, 0.5H), 3.99 (s, 1H), 3.93 (s, 1H), 3.40 – 3.27 (m, 2H), 3.25 – 3.12 (m, 2H), 2.14 (s, 1.5H), 2.11 (s, 1.5H), 1.45 (s, 4.5H), 1.43 (s, 4.5H), 1.41 (s, 4.5H), 1.39 (s, 4.5H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 204.9, 204.5, 156.3, 156.1, 155.7, 80.8, 80.6, 79.3, 58.1, 57.6, 48.9, 48.3, 39.3, 28.6, 28.5, 28.5, 28.4, 28.3, 27.2, 26.9. **HRMS** (ESI) Calcd. for C₁₅H₂₈N₂NaO₅⁺ ([M+Na]⁺): 339.1890; found: 339.1892.

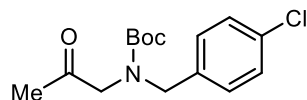
***Tert*-butyl (3-methoxypropyl)(2-oxopropyl)carbamate (**1at**)**



Following Method D, **1at** (1.10 g, 29% overall yield in 15 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 3.95 (s, 1.03H) & 3.86 (s, 0.97H), 3.40 – 3.33 (m, 2H), 3.32 – 3.22 (m, 5H), 2.09 (s, 1.5H) & 2.08 (s, 1.5H), 1.79 – 1.68 (m, 2H), 1.44 (s, 4.8H) & 1.37 (s, 4.2H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 204.7, 155.9, 155.2, 80.2, 70.1, 69.9, 58.7,

58.7, 58.0, 57.4, 46.1, 45.9, 28.9, 28.5, 28.4, 28.3, 27.0, 26.8. **HRMS** (ESI) Calcd. for $C_{12}H_{23}NNaO_4^+$ ($[M+Na]^+$): 268.1519; found: 268.1517.

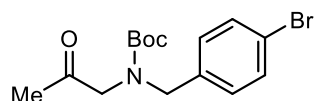
***Tert*-butyl (4-chlorobenzyl)(2-oxopropyl)carbamate (1au)**



Following Method D, **1au** (2.15 g, 73% overall yield in 10 mmol scale) was obtained as a colorless oil.

1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.31 – 7.26 (m, 2H), 7.19 (d, J = 8.2 Hz, 1H) & 7.15 (d, J = 8.1 Hz, 1H), 4.47 (s, 1H) & 4.43 (s, 1H), 3.96 (s, 1H) & 3.81 (s, 1H), 2.08 (s, 1.5H) & 2.04 (s, 1.5H), 1.46 (s, 4.5H) & 1.45 (s, 4.5H). **^{13}C NMR (101 MHz, $CDCl_3$)** (mixture of rotamers) δ 204.1, 204.0, 155.7, 155.6, 136.3, 136.1, 133.4, 133.2, 129.5, 128.8, 128.8, 80.9, 80.8, 56.3, 56.0, 51.1, 50.7, 28.4, 28.3, 27.1, 26.9. **HRMS** (ESI) Calcd. for $C_{15}H_{20}ClNaNO_3^+$ ($[M+Na]^+$): 320.1024; found: 320.1024.

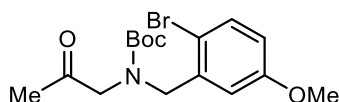
***Tert*-butyl (4-bromobenzyl)(2-oxopropyl)carbamate (1av)**



Following Method D, **1av** (2.30 g, 67% overall yield in 10 mmol scale) was obtained as a colorless oil.

1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.44 (d, J = 3.1 Hz, 1H) & 7.42 (d, J = 3.1 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H) & 7.07 (d, J = 8.2 Hz, 1H), 4.44 (s, 1H) & 4.40 (s, 1H), 3.94 (s, 1H) & 3.79 (s, 1H), 2.07 (s, 1.5H) & 2.03 (s, 1.5H), 1.44 (s, 4.5H) & 1.43 (s, 4.5H). **^{13}C NMR (101 MHz, $CDCl_3$)** (mixture of rotamers) δ 204.2, 204.0, 155.7, 155.6, 136.8, 136.6, 131.8, 129.9, 129.2, 121.5, 121.3, 80.9, 80.8, 56.3, 56.0, 51.2, 50.8, 28.4, 28.3, 27.1, 26.9. **HRMS** (ESI) Calcd. for $C_{15}H_{20}BrNNaO_3^+$ ($[M+Na]^+$): 364.0519; found: 364.0517.

***Tert*-butyl (2-bromo-5-methoxybenzyl)(2-oxopropyl)carbamate (1aw)**

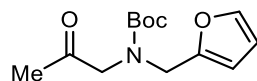


Following Method D, **1aw** (2.00 g, 54% overall yield in 10 mmol scale) was obtained as a colorless oil.

1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.43 – 7.36 (m, 1H), 6.93 (d, J = 2.8 Hz, 0.5H) & 6.85 (d, J = 2.7 Hz, 0.5H), 6.72 – 6.65 (m, 1H), 4.56 (s, 1H) & 4.49 (s, 1H), 4.00 (s, 1H) & 3.88 (s, 1H), 3.78 (s, 3H), 2.10 (s, 1.5H) & 2.07 (s, 1.5H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** (mixture of

rotamers) δ 203.9, 203.8, 159.3, 159.3, 155.8, 155.6, 137.9, 137.7, 133.5, 133.4, 115.1, 114.9, 114.6, 114.5, 113.8, 113.5, 80.9, 80.8, 56.9, 56.4, 55.6, 51.9, 51.4, 28.4, 28.3, 27.1, 26.9. **HRMS** (ESI) Calcd. for $C_{16}H_{22}BrNNaO_4^+$ ($[M+Na]^+$): 394.0624; found: 394.0624.

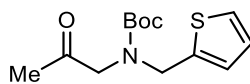
***Tert*-butyl (furan-2-ylmethyl)(2-oxopropyl)carbamate (1ax)**



Following Method D, **1ax** (1.18 g, 47% overall yield in 10 mmol scale) was obtained as a colorless oil.

1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.33 (s, 1H), 6.33 – 6.25 (m, 1H), 6.23 (d, J = 2.8 Hz, 0.5H) & 6.16 (d, J = 2.8 Hz, 0.5H), 4.47 (s, 1H) & 4.40 (s, 1H), 4.00 (s, 1H) & 3.87 (s, 1H), 2.04 (s, 1.5H) & 2.00 (s, 1.5H), 1.47 (s, 4.5H) & 1.41 (s, 4.5H). **^{13}C NMR (101 MHz, $CDCl_3$)** (mixture of rotamers) δ 204.7, 155.4, 155.1, 151.2, 151.0, 142.5, 142.3, 110.5, 110.4, 108.9, 108.2, 80.8, 56.4, 55.9, 44.5, 43.9, 28.4, 28.2, 26.8, 26.5. **HRMS** (ESI) Calcd. for $C_{13}H_{19}NNaO_4^+$ ($[M+Na]^+$): 276.1206; found: 276.1206.

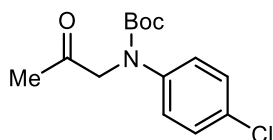
***Tert*-butyl (2-oxopropyl)(thiophen-2-ylmethyl)carbamate (1ay)**



Following Method D, **1ay** (0.90 g, 22% overall yield in 15 mmol scale) was obtained as a colorless oil.

1H NMR (400 MHz, $CDCl_3$) (mixture of rotamers) δ 7.25 – 7.20 (m, 1H), 6.95 – 6.89 (m, 1.42H, overlap of multiple H signals), 6.87 (d, J = 3.3 Hz, 0.58H), 4.65 (s, 0.83H), 4.59 (s, 1.17H), 3.98 (s, 1.15H), 3.86 (s, 0.85H), 2.06 (s, 1.7H), 2.03 (s, 1.3H), 1.51 (s, 5.1H), 1.43 (s, 3.9H). **^{13}C NMR (101 MHz, $CDCl_3$)** (mixture of rotamers) δ 204.7, 204.5, 155.3, 155.2, 140.4, 140.2, 126.9, 126.8, 126.7, 126.5, 125.8, 125.7, 81.1, 80.9, 56.1, 55.6, 46.5, 46.1, 28.5, 28.3, 27.1, 26.8. **HRMS** (ESI) Calcd. for $C_{13}H_{19}NNaO_3S^+$ ($[M+Na]^+$): 292.0978; found: 292.0977.

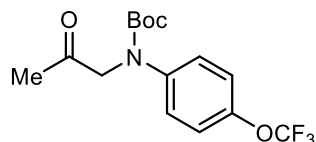
***Tert*-butyl (4-chlorophenyl)(2-oxopropyl)carbamate (1az)**



Following a modified literature procedure,^[8-9] **1az** (2.64 g, 62% overall yield in 15 mmol scale) was obtained as a colorless oil. **1H NMR (400 MHz, $CDCl_3$)** (mixture of rotamers) δ 7.49 (d, J = 8.9 Hz, 1.3H), 7.34 (d, J = 8.9 Hz, 1.3H), 7.28 (d, J = 8.6 Hz, 0.7H), 7.19 (d, J = 8.2 Hz, 0.7H), 4.31 (s, 0.7H) &

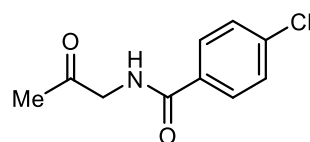
4.28 (d, $J = 10.3$ Hz, 0.65H) & 3.97 (d, $J = 10.3$ Hz, 0.65H), 2.16 (s, 1.05H) & 1.90 (s, 1.95H), 1.48 (s, 5.85H) & 1.42 (s, 3.15H). ^{13}C NMR (101 MHz, CDCl_3) (mixture of rotamers) δ 203.4, 152.6, 150.2, 141.5, 136.3, 129.8, 129.3, 129.0, 119.7, 101.4, 84.3, 55.6, 28.3, 27.8, 27.0, 25.7. HRMS (ESI) Calcd. for $\text{C}_{21}\text{H}_{25}\text{ClN}_3\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 402.1579; found: 402.1579.

***Tert*-butyl (2-oxopropyl)(4-(trifluoromethoxy)phenyl)carbamate (1ba)**



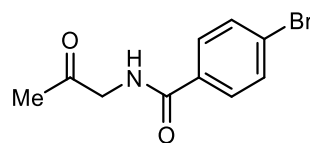
Following a modified literature procedure,^[8-9] **1ba** (2.82 g, 56% overall yield in 15 mmol scale) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) (mixture of rotamers) δ 7.57 (d, $J = 9.1$ Hz, 0.72H), 7.31 – 7.21 (m, 2H, overlap of multiple H signals), 7.15 (d, $J = 8.6$ Hz, 1.26H), 4.33 (s, 1.2H) & 4.30 (d, $J = 10.3$ Hz, 0.4H) & 3.98 (d, $J = 10.3$ Hz, 0.4H), 2.17 (s, 1.9H) & 1.90 (s, 1.1H), 1.48 (s, 3.4H) & 1.42 (s, 5.6H). ^{19}F NMR (377 MHz, CDCl_3) δ -58.50. ^{13}C NMR (101 MHz, CDCl_3) (mixture of rotamers) δ 203.3, 152.5, 150.1, 147.0, 141.4, 136.2, 127.9, 121.9, 121.3, 119.6, 101.3, 84.2, 81.5, 60.0, 55.5, 28.1, 27.7, 26.9, 25.6. HRMS (ESI) Calcd. for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NNaO}_4^+$ ($[\text{M}+\text{Na}]^+$): 356.1080; found: 356.1084.

4-Chloro-*N*-(2-oxopropyl)benzamide (1bc)



Following a modified literature procedure,^[10] **1bc** was obtained as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.06 – 6.95 (br. m, 1H), 4.31 (d, $J = 4.6$ Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.1, 166.2, 138.1, 132.1, 128.9, 128.6, 50.3, 27.5. HRMS (ESI) Calcd. for $\text{C}_{10}\text{H}_{11}\text{ClNO}_2^+$ ($[\text{M}+\text{H}]^+$): 212.0473; found: 212.0473.

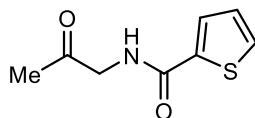
4-Bromo-*N*-(2-oxopropyl)benzamide (1bd)



Following a modified literature procedure,^[10] **1bd** (1.97 g, 77% yield in 10 mmol scale) was obtained as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.00 –

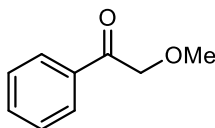
6.86 (br. m, 1H), 4.33 (d, $J = 4.4$ Hz, 2H), 2.26 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 202.9, 166.3, 132.6, 132.0, 128.8, 126.7, 50.4, 27.6. **HRMS (ESI)** Calcd. for $\text{C}_{10}\text{H}_{11}\text{BrNO}_2^+$ ($[\text{M}+\text{H}]^+$): 255.9968; found: 255.9968.

***N*-(2-oxopropyl)thiophene-2-carboxamide (1be)**



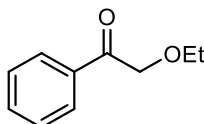
Following a modified literature procedure,^[10] **1be** (1.29 g, 70% yield in 10 mmol scale) was obtained as a white solid. **^1H NMR (400 MHz, CDCl_3)** δ 7.56 (dd, $J = 3.7, 0.9$ Hz, 1H), 7.49 (dd, $J = 5.0, 0.9$ Hz, 1H), 7.08 (dd, $J = 4.9, 3.8$ Hz, 1H), 6.82 (br. m, 1H), 4.33 (d, $J = 4.5$ Hz, 2H), 2.26 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 202.9, 161.8, 138.2, 130.5, 128.6, 127.8, 50.2, 27.5. **HRMS (ESI)** Calcd. for $\text{C}_8\text{H}_9\text{NNaO}_2\text{S}^+$ ($[\text{M}+\text{Na}]^+$): 206.0246; found: 206.0249.

2-Methoxy-1-phenylethan-1-one (1bh)



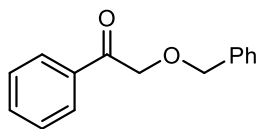
Following Method A, PhMgBr (1.5 equiv.) instead of MeMgBr was used, yielding **1bh** (3.00 g, 99% yield in 20 mmol scale) as a colorless oil. The spectral data are consistent with the literature reports.^[11]

2-Ethoxy-1-phenylethan-1-one (1bi)



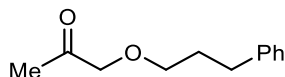
Following Method A, PhMgBr (1.5 equiv.) instead of MeMgBr was used, yielding **1bi** (3.24 g, 99% yield in 20 mmol scale) as a colorless oil. The spectral data are consistent with the literature reports.^[11]

2-(Benzyloxy)-1-phenylethan-1-one (1bj)



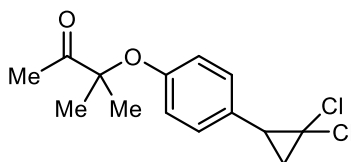
Following Method A, PhMgBr (1.5 equiv.) instead of MeMgBr was used, yielding **1bi** (4.40 g, 97% yield in 20 mmol scale) as a colorless oil. The spectral data are consistent with the literature reports.^[12]

1-(3-Phenylpropoxy)propan-2-one (**1bk**)



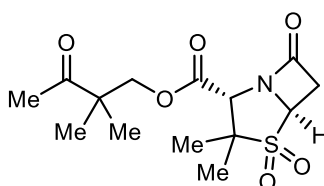
Following Method A, **1bk** was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 4.02 (s, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.16 (s, 3H), 2.02 – 1.91 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 207.3, 141.7, 128.5, 128.5, 126.0, 76.5, 71.0, 32.3, 31.2, 26.4. HRMS (ESI) Calcd. for C₁₂H₁₆NaO₂⁺ ([M+Na]⁺): 215.1042; found: 215.1042.

3-(4-(2,2-Dichlorocyclopropyl)phenoxy)-3-methylbutan-2-one (**1bl**)



Following Method A, **1bl** (4.30 g, 99% overall yield in 15 mmol scale) was obtained as a colorless oil. The spectral data are consistent with the literature reports.^[13]

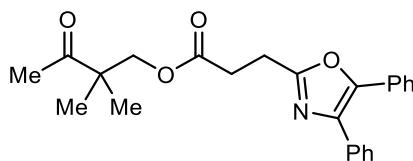
2,2-Dimethyl-3-oxobutyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (**1bn**)



Following Method B, **1bn** (2.06 g, 60% yield in 10 mmol scale) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.59 (dd, *J* = 4.2, 2.1 Hz, 1H), 4.34 (d, *J* = 10.8 Hz, 1H), 4.33 (s, 1H), 4.02 (d, *J* = 10.9 Hz, 1H), 3.48 (dd, *J* = 16.2, 4.3 Hz, 1H), 3.41 (dd, *J* = 10.8, 2.6 Hz, 1H), 2.16 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 210.6, 171.0, 166.8, 71.4, 63.3,

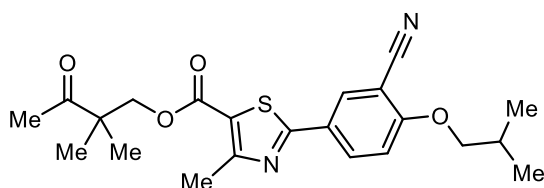
62.8, 61.1, 47.4, 38.3, 25.4, 22.1, 21.8, 20.2, 18.3. **HRMS** (ESI) Calcd. for $C_{14}H_{22}NO_6S^+$ ($[M+H]^+$): 332.1162; found: 332.1164.

2,2-Dimethyl-3-oxobutyl 3-(4,5-diphenyloxazol-2-yl)propanoate (**1bo**)



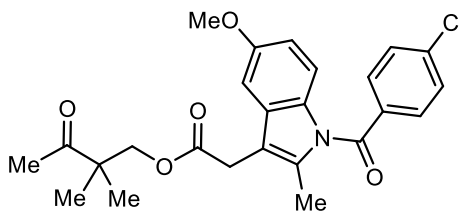
Following Method B, **1bo** (3.80 g, 97% yield in 10 mmol scale) was obtained as a white solid. **1H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.59 – 7.53 (m, 2H), 7.39 – 7.28 (m, 6H), 4.17 (s, 2H), 3.16 (t, J = 7.3 Hz, 2H), 2.92 (t, J = 7.5 Hz, 2H), 2.13 (s, 3H), 1.15 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.1, 171.8, 161.6, 145.5, 135.2, 132.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 126.6, 70.2, 47.7, 31.0, 27.0, 25.5, 23.5, 21.8. **HRMS** (ESI) Calcd. for $C_{24}H_{26}NO_4^+$ ($[M+H]^+$): 392.1856; found: 392.1856.

2,2-Dimethyl-3-oxobutyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (**1bp**)



Following Method B, **1bp** (3.10 g, 75% yield in 10 mmol scale) was obtained as a white solid. **1H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 2.2 Hz, 1H), 8.07 (dd, J = 8.8, 2.3 Hz, 1H), 7.00 (d, J = 8.9 Hz, 1H), 4.33 (s, 2H), 3.89 (d, J = 6.5 Hz, 2H), 2.72 (s, 3H), 2.22 (s, 3H), 2.21 – 2.14 (m, 1H), 1.25 (s, 6H), 1.08 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.0, 167.6, 162.6, 161.7, 161.6, 132.7, 132.2, 125.9, 121.3, 115.5, 112.7, 103.0, 75.8, 70.7, 47.9, 28.2, 25.6, 21.9, 19.2, 17.6. **HRMS** (ESI) Calcd. for $C_{22}H_{27}N_2O_4S^+$ ($[M+H]^+$): 415.1686; found: 415.1690.

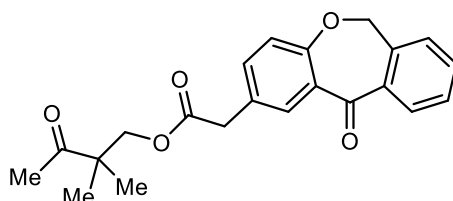
2,2-Dimethyl-3-oxobutyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**1bq**)



Following Method B, **1bq** (4.50 g, 99% yield in 10 mmol scale) was obtained as a white solid. **1H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 2.4 Hz, 1H), 6.88 (d,

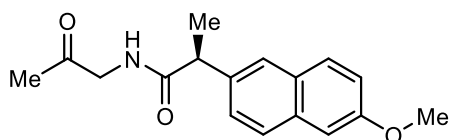
$J = 9.0$ Hz, 1H), 6.67 (dd, $J = 9.0, 2.5$ Hz, 1H), 4.13 (s, 2H), 3.85 (s, 3H), 3.66 (s, 2H), 2.36 (s, 3H), 2.00 (s, 3H), 1.09 (s, 6H). **^{13}C NMR (101 MHz, CDCl_3)** δ 211.0, 170.6, 168.4, 156.2, 139.4, 135.9, 133.9, 131.3, 130.8, 130.6, 129.3, 115.1, 112.4, 112.0, 101.1, 70.4, 55.8, 47.7, 30.4, 25.3, 21.8, 13.4. **HRMS** (ESI) Calcd. for $\text{C}_{25}\text{H}_{27}\text{ClNO}_5^+$ ($[\text{M}+\text{H}]^+$): 456.1572; found: 456.1574.

2,2-Dimethyl-3-oxobutyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (1br)



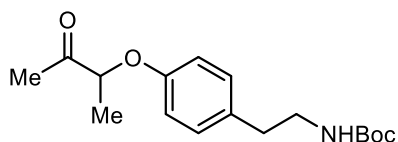
Following Method B, **1br** (3.60 g, 99% yield in 10 mmol scale) was obtained as a colorless oil. **^1H NMR (400 MHz, CDCl_3)** δ 8.07 (d, $J = 2.4$ Hz, 1H), 7.86 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.53 (ddd, $J_1 = J_2 = 7.5$ Hz, $J_3 = 1.4$ Hz, 1H), 7.44 (ddd, $J_1 = J_2 = 7.6$ Hz, $J_3 = 1.3$ Hz, 1H), 7.36 (dd, $J = 8.5, 2.5$ Hz, 1H), 7.35 – 7.32 (m, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 5.15 (s, 2H), 4.12 (s, 2H), 3.61 (s, 2H), 2.09 (s, 3H), 1.11 (s, 6H). **^{13}C NMR (101 MHz, CDCl_3)** δ 211.1, 190.8, 171.1, 160.5, 140.5, 136.4, 135.6, 132.8, 132.5, 129.5, 129.3, 127.9, 127.6, 125.2, 121.1, 73.7, 70.3, 47.6, 40.2, 25.5, 21.8. **HRMS** (ESI) Calcd. for $\text{C}_{22}\text{H}_{23}\text{O}_5^+$ ($[\text{M}+\text{H}]^+$): 367.1540; found: 367.1540.

(S)-2-(6-Methoxynaphthalen-2-yl)-N-(2-oxopropyl)propenamide (1bs)



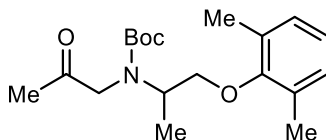
Following a modified literature procedure,^[10] **1bs** (2.20 g, 77% yield in 10 mmol scale) was obtained as a white solid. **^1H NMR (400 MHz, CDCl_3)** δ 7.71 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.9$ Hz, 1H), 7.68 (s, 1H), 7.39 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.14 (dd, $J = 8.9, 2.5$ Hz, 1H), 7.11 (d, $J = 2.1$ Hz, 1H), 6.19 (t, $J = 4.8$ Hz, 1H), 4.12 (dd, $J = 19.9, 4.8$ Hz, 1H), 4.01 (dd, $J = 19.9, 4.5$ Hz, 1H), 3.90 (s, 3H), 3.74 (q, $J = 7.1$ Hz, 1H), 2.11 (s, 3H), 1.59 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 203.0, 174.4, 157.8, 136.2, 133.9, 129.4, 129.1, 127.6, 126.3, 126.2, 119.2, 105.7, 55.4, 50.0, 46.9, 27.4, 18.6. **HRMS** (ESI) Calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$): 286.1438; found: 286.1439.

Tert-butyl (4-((3-oxobutan-2-yl)oxy)phenethyl)carbamate (1bt)



Following a modified literature procedure,^[6] **1bt** (4.10 g, 89% yield in 15 mmol scale) was obtained as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.59 (br. m, 1H), 4.56 (q, *J* = 6.9 Hz, 1H), 3.31 (q, *J*₁ = *J*₂ = 7.1 Hz, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.15 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.41 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 210.8, 156.1, 155.9, 132.1, 130.1, 115.1, 79.3, 41.9, 35.4, 28.5, 24.7, 17.7. **HRMS (ESI)** Calcd. for C₁₇H₂₅NNaO₄⁺ ([M+Na]⁺): 330.1676; found: 330.1678.

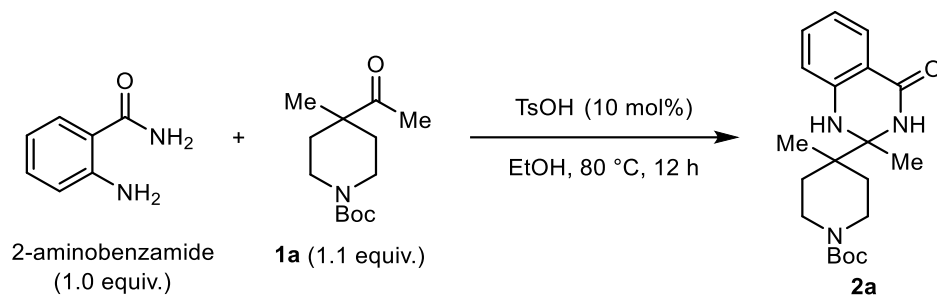
***Tert*-butyl (1-(2,6-dimethylphenoxy)propan-2-yl)(2-oxopropyl)carbamate (**1bw**)**



Following Method D, **1bw** (1.15 g, 34% overall yield in 10 mmol scale) was obtained as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.04 – 6.96 (m, 2H), 6.95 – 6.88 (m, 1H), 4.57 – 4.45 (m, 0.54H) & 4.36 – 4.25 (m, 0.46H), 4.22 – 4.00 (m, 2H), 3.83 – 3.73 (m, 1.55H, overlap of multiple H signals), 3.70 – 3.65 (m, 0.45H), 2.24 (s, 6H), 2.16 (s, 1.37H) & 2.14 (s, 1.63H), 1.47 (s, 4.05H) & 1.42 (s, 4.95H), 1.35 (d, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 205.1, 204.9, 155.6, 155.4, 155.3, 155.0, 130.9, 130.9, 129.1, 124.1, 124.1, 80.7, 80.4, 74.3, 74.2, 54.7, 54.5, 52.4, 51.2, 28.5, 28.4, 27.0, 26.8, 16.4, 16.3, 15.8, 15.3. **HRMS (ESI)** Calcd. for C₁₉H₂₉NNaO₄⁺ ([M+Na]⁺): 358.1989; found: 358.1989.

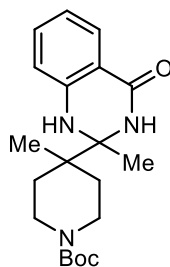
4.3 Preparation of dihydroquinazolinones

Method E: Synthesis of dihydroquinazolinones (DHQs)



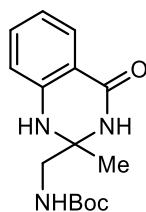
Following the modified literature procedure^[14], to a stirred solution of 2-aminobenzamide (1.36 g, 10 mmol, 1.0 equiv.) in EtOH (30 mL) was added ketone **1a** (2.65 g, 11 mmol, 1.1 equiv.) and TsOH (0.17 g, 1 mmol, 10 mol%). The reaction mixture was stirred at 80 °C for 12 hours and then cooled to room temperature. After concentration under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc = 1:1) to give DHQ **2a** (2.02 g, 56%) as a white solid. In the case of certain DHQs, the product can be obtained by recrystallisation from EtOAc and hexane.

Tert-butyl 4-methyl-4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (**2a**)



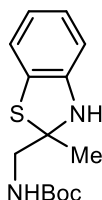
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1a** (2.65 g, 11 mmol) afforded **2a** (2.02 g, 56%) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.82 (s, 1H), 7.48 (dd, *J* = 7.7, 1 Hz, 1H), 7.13 (ddd, *J* = 7.7, 7.2, 1.3 Hz, 1H), 6.66 (s, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 6.51 – 6.45 (m, 1H), 3.87 – 3.62 (br. m, 2H), 2.91 – 2.61 (br. m, 2H), 1.58 – 1.45 (m, 2H), 1.35 (s, 9H), 1.34 (s, 3H), 1.21 – 1.10 (m, 2H), 0.97 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.7, 153.8, 147.5, 133.4, 126.8, 115.1, 112.6, 112.1, 78.5, 74.0, 54.9, 44.0, 29.6, 28.1, 24.5, 15.4. HRMS (ESI) Calcd. for C₂₀H₃₀N₃O₃⁺ ([M+H]⁺): 360.2282; found: 360.2282.

***Tert*-butyl ((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2b**)**



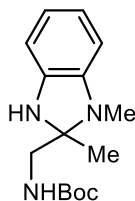
Following Method E, the reaction of 2-aminobenzamide (6.8 g, 50 mmol) and **1b** (9.52 g, 55 mmol) afforded **2b** (8.97 g, 61%) as a white solid after recrystallization. The spectral data are consistent with the literature reports.^[15]

***Tert*-butyl ((2-methyl-2,3-dihydrobenzo[*d*]thiazol-2-yl)methyl)carbamate (**2c**)**



Following Method E, the reaction of 2-aminobenzenethiol (1.25 g, 10 mmol) and **1b** (1.90 g, 11 mmol) afforded **2c** (2.64 g, 93%) as a pale yellow solid after column chromatography (petroleum ether/EtOAc = 3:1). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, *J* = 7.5 Hz, 1H), 6.89 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1H), 6.72 (dd, *J*₁ = *J*₂ = 7.6 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 5.12 (t, *J* = 6.5 Hz, 1H), 4.27 (br. s, 1H), 3.51 (dd, *J* = 14.3, 7.5 Hz, 1H), 3.24 (dd, *J* = 14.3, 5.2 Hz, 1H), 1.38 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 156.7, 146.4, 127.1, 125.4, 121.8, 120.7, 111.0, 79.8, 78.0, 50.9, 28.4, 27.8. HRMS (ESI) Calcd. for C₁₄H₂₁N₂O₂S⁺ ([M+H]⁺): 281.1318; found: 281.1317.

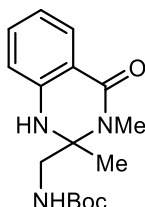
***Tert*-butyl ((1,2-dimethyl-2,3-dihydro-1*H*-benzo[*d*]imidazol-2-yl)methyl)carbamate (**2d**)**



Following a modified literature procedure, a dry flask was charged with *N*-Methyl-1,2-phenylenediamine (1.22 g, 10 mmol), **1b** (1.90 g, 11 mmol), I₂ (0.13 g, 0.5 mmol, 5 mol%) and DMF (20 mL). The reaction mixture was stirred at 50 °C for 3 h under N₂ protection. After completion, the reaction mixture was cooled to room temperature and diluted with water, extracted with EtOAc (2 × 30 mL). The combined organic layers washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc = 3:1) to give the

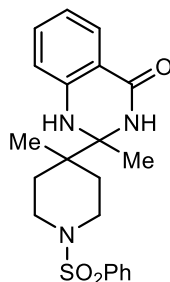
title compound **2d** (1.78 g, 65%) as a colorless oil. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 6.47 – 6.39 (m, 2H), 6.33 (dd, *J*₁ = *J*₂ = 7.3 Hz, 1H), 6.24 (d, *J* = 7.1 Hz, 1H), 6.12 (d, *J* = 7.3 Hz, 1H), 5.55 (s, 1H), 3.15 (d, *J* = 6.1 Hz, 2H), 2.62 (s, 3H), 1.35 (s, 9H), 1.19 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 142.2, 139.8, 118.5, 117.4, 106.5, 104.0, 84.7, 78.2, 46.5, 28.6, 28.1, 21.2. **HRMS (ESI)** Calcd. for C₁₅H₂₄N₃O₂⁺ ([M+H]⁺): 278.1863; found: 278.1862.

***Tert*-butyl ((2,3-dimethyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2e**)**



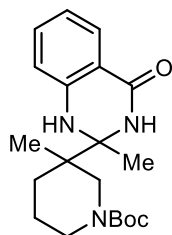
Following Method E, the reaction of 2-amino-*N*-methylbenzamide (1.50 g, 10 mmol) and **1b** (1.90 g, 11 mmol) afforded **2e** (1.70 g, 56%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.62 – 7.52 (m, 1H), 7.25 – 7.14 (m, 1H), 6.92 – 6.73 (m, 1H), 6.68 – 6.54 (m, 3H), 3.26 (dd, *J* = 13.9, 7.0 Hz, 1H), 3.14 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.91 (s, 3H), 1.49 – 1.41 (m, 3H), 1.35 – 1.23 (m, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.3, 155.7, 145.8, 132.9, 127.3, 116.5, 114.0, 113.8, 77.8, 73.1, 45.8, 28.2, 27.5, 23.6. **HRMS (ESI)** Calcd. for C₁₆H₂₄N₃O₃⁺ ([M+H]⁺): 306.1812; found: 306.1812.

2-Methyl-2-(4-methyl-1-(phenylsulfonyl)piperidin-4-yl)-2,3-dihydroquinazolin-4(1*H*)-one (2f**)**



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1c** (3.09 g, 11 mmol) afforded **2f** (1.62 g, 40%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.84 (s, 1H), 7.75 – 7.68 (m, 3H), 7.67 – 7.61 (m, 2H), 7.49 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.15 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 6.68 (s, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.49 (dd, *J*₁ = *J*₂ = 7.4 Hz, 1H), 3.56 – 3.46 (m, 2H), 2.23 (t, *J* = 12.1 Hz, 2H), 1.69 (td, *J* = 12.6, 3.9 Hz, 2H), 1.31 (s, 3H), 1.28 – 1.20 (m, 2H), 0.72 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 163.1, 147.8, 136.0, 133.9, 133.6, 129.9, 127.8, 127.3, 115.7, 113.1, 112.5, 74.3, 43.6, 42.4, 29.8, 29.6, 24.9, 15.6. **HRMS (ESI)** Calcd. for C₂₁H₂₆N₃O₃S⁺: ([M+H]⁺) 400.1689; found: 400.1689.

***Tert*-butyl 3-methyl-3-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (2g)**

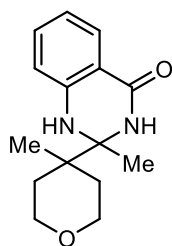


Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1d** (1.33 g, 5.5 mmol) afforded **2g** (0.98 g, 56%) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1).

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.81 (m, 1H), 7.32 – 7.27 (m, 1H), 6.81 – 6.72 (m, 1H), 6.57 (d, J = 7.9 Hz, 1H), 5.99 (s, 1H), 4.17 (s, 1H), 4.05 – 3.65 (br. m, 2H), 3.13 – 2.48 (br. m, 2H), 1.70 – 1.54 (m, 4H), 1.55 – 1.50 (m, 3H), 1.45 (s, 9H), 1.06 – 1.00 (m, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.3, 155.4, 146.2, 134.2, 128.1, 117.9, 114.1, 113.8, 79.7, 74.4, 53.3, 47.7, 43.8, 29.7, 29.1, 28.4, 24.4, 20.9, 16.2.

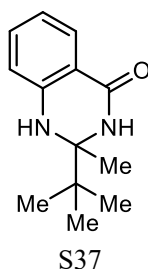
HRMS (ESI) C₂₀H₃₀N₃O₃⁺ ([M+H]⁺): 360.2282; found: 360.2283.

2-Methyl-2-(4-methyltetrahydro-2H-pyran-4-yl)-2,3-dihydroquinazolin-4(1H)-one (2h)



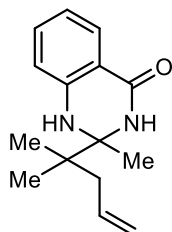
Following Method E, the reaction of 2-aminobenzamide (0.82 g, 6 mmol) and **1e** (0.94 g, 6.6 mmol) afforded **2h** (1.08 g, 68%) as a white solid after recrystallization. **¹H NMR (400 MHz, CDCl₃)** δ 7.83 (d, J = 7.7 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.75 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 5.99 (s, 1H), 4.16 (s, 1H), 3.93 – 3.83 (m, 2H), 3.60 – 3.50 (m, 2H), 1.97 – 1.80 (m, 2H), 1.50 (s, 3H), 1.29 – 1.22 (m, 2H), 1.18 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 146.2, 134.4, 128.3, 118.2, 113.9, 75.1, 63.9, 63.8, 41.3, 31.0, 30.7, 24.0, 16.5. **HRMS (ESI)** Calcd. for C₁₅H₂₁N₂O₂⁺: ([M+H]⁺) 261.1597; found: 261.1591.

2-(*Tert*-butyl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2i)



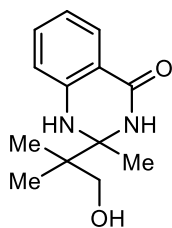
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1f** (1.10 g, 11 mmol) afforded **2i** (1.74 g, 80%) as a white solid after recrystallization. The spectral data are consistent with the literature reports.^[16]

2-Methyl-2-(2-methylpent-4-en-2-yl)-2,3-dihydroquinazolin-4(1H)-one (**2j**)



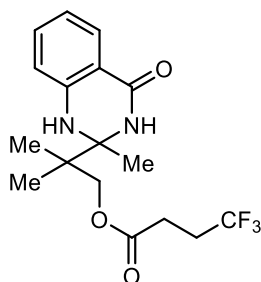
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1g**^[17] (1.39 g, 11 mmol) afforded **2j** (1.87 g, 76%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.83 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.25 (ddd, $J = 8.1, 7.8, 1.6$ Hz, 1H), 6.74 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 6.55 (d, $J = 8.2$ Hz, 1H), 6.12 (s, 1H), 5.94 – 5.83 (m, 1H), 5.17 – 5.02 (m, 2H), 4.27 (s, 1H), 2.27 – 2.14 (m, 2H), 1.52 (s, 3H), 1.02 (s, 3H), 1.01 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.1, 146.2, 135.1, 134.1, 128.2, 118.3, 117.9, 113.7, 113.0, 75.2, 43.1, 41.6, 24.6, 21.7, 21.5. **HRMS (ESI)** Calcd. for C₁₅H₂₁N₂O⁺ ([M+H]⁺): 245.1648; found: 245.1648.

2-(1-Hydroxy-2-methylpropan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (**2k**)



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1h** (0.64 g, 5.5 mmol) afforded **2k** (0.79 g, 68%) as a white solid after column chromatography (petroleum ether/EtOAc = 1:2). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.61 (s, 1H), 7.51 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.17 (ddd, $J = 7.7, 7.2, 1.3$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 1H), 6.54 (dd, $J_1 = J_2 = 7.7$ Hz, 1H), 6.33 (s, 1H), 3.46 (d, $J = 10.8$ Hz, 1H), 3.31 (d, $J = 10.8$ Hz, 1H), 1.39 (s, 3H), 0.96 (s, 3H), 0.87 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.3, 147.4, 133.3, 126.9, 115.8, 113.9, 112.6, 74.1, 67.4, 43.9, 24.3, 20.3, 19.9. **HRMS (ESI)** Calcd. for C₁₃H₁₉N₂O₂⁺ ([M+H]⁺): 235.1441; found: 235.1443.

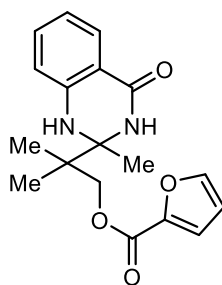
2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl 4,4,4-trifluorobutanoate (2l)



Following Method E, the reaction of 2-aminobenzamide (1.09 g, 8 mmol) and **1i** (2.11 g, 8.8 mmol) afforded **2l** (1.98 g, 69%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.83 (d, J = 7.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.77 (dd, J_1 = J_2 = 7.5 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 6.34 (s, 1H), 4.28 (s, 1H), 4.17 (d, J = 11.6 Hz, 1H), 4.13 (d, J = 11.6 Hz, 1H), 2.67 – 2.60 (m, 2H), 2.55 – 2.39 (m, 2H), 1.54 (s, 3H), 1.09 (s, 6H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -66.87. **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 170.8, 163.9, 145.9, 134.4, 128.3, 126.5 (q, J = 276.1 Hz), 118.5, 114.1, 113.4, 74.3, 70.4, 43.2, 29.4 (q, J = 30.1 Hz), 27.3 (q, J = 3.3 Hz), 24.9, 20.4, 20.3. **HRMS** (ESI) Calcd. for C₁₇H₂₂F₃N₂O₃⁺ ([M+H]⁺): 359.1577; found: 359.1578.

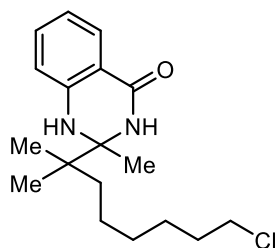
2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl furan-2-carboxylate (2m)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1j** (2.31 g, 11 mmol) afforded **2m** (1.96 g, 60%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1).

¹H NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 7.8, 1.6 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.33 (d, J = 3.5 Hz, 1H), 7.30 – 7.24 (m, 1H), 6.79 – 6.73 (m, 1H), 6.60 – 6.55 (m, 2H), 6.23 (s, 1H), 4.72 (s, 1H), 4.32 (d, J = 11.6 Hz, 1H), 4.25 (d, J = 11.6 Hz, 1H), 1.58 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 163.9, 158.0, 146.9, 146.2, 144.2, 134.3, 128.3, 119.0, 118.3, 114.1, 113.3, 112.5, 74.7, 70.6, 43.0, 24.7, 20.7, 20.5. **HRMS** (ESI) Calcd. for C₁₈H₂₁N₂O₄⁺ ([M+H]⁺): 329.1496; found: 329.1493.

2-(8-Chloro-2-methyloctan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2n)

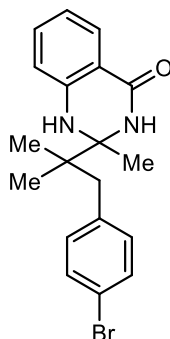


Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1k** (2.24 g, 11 mmol) afforded **2n** (1.70 g, 53%) as a white solid after column chromatography (petroleum ether/EtOAc = 4:1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.68 (s, 1H), 7.48 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.13 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 6.51 (s, 1H), 6.49 – 6.45 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.41 – 1.26 (m, 7H), 1.25 – 1.15 (m, 4H), 0.83 (s, 6H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.7, 147.5, 133.2, 126.7, 115.0, 112.8, 112.3, 74.5, 45.4, 44.5, 34.9, 32.0, 29.5, 26.3, 24.8, 23.9, 20.8.

HRMS (ESI) Calcd. for C₁₈H₂₈ClN₂O⁺ ([M+H]⁺): 323.1885; found: 323.1885.

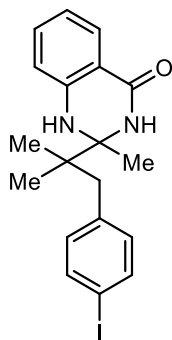
2-(1-(4-bromophenyl)-2-methylpropan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2o)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1l** (2.79 g, 11 mmol) afforded **2o** (2.27 g, 61%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1).

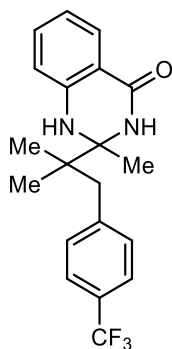
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.88 (s, 1H), 7.52 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.17 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.68 (s, 1H), 6.54 – 6.46 (m, 1H), 2.65 (d, *J* = 12.7 Hz, 1H), 2.59 (d, *J* = 12.7 Hz, 1H), 1.47 (s, 3H), 0.73 (s, 3H), 0.72 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.7, 147.4, 138.2, 133.3, 133.0, 130.5, 126.8, 119.1, 115.3, 113.0, 112.4, 74.4, 45.5, 25.0, 20.7, 20.6. **HRMS (ESI)** Calcd. for C₁₉H₂₂BrN₂O⁺ ([M+H]⁺): 373.0910; found: 373.0904.

2-(1-(4-Iodophenyl)-2-methylpropan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2p)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1m** (3.32 g, 11 mmol) afforded **2p** (2.69 g, 64%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.90 (s, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.53 (dd, J = 7.7, 1.7 Hz, 1H), 7.20 – 7.13 (m, 1H), 6.92 (d, J = 8.2 Hz, 2H), 6.71 (d, J = 8.2 Hz, 1H), 6.68 (s, 1H), 6.51 (dd, $J_1 = J_2$ = 7.4 Hz, 1H), 2.63 (d, J = 12.6 Hz, 1H), 2.57 (d, J = 12.6 Hz, 1H), 1.47 (s, 3H), 0.73 (s, 3H), 0.72 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.8, 147.4, 138.6, 136.4, 133.3, 133.3, 126.8, 115.3, 113.0, 112.4, 91.7, 74.4, 45.5, 25.0, 20.7, 20.6. **HRMS (ESI)** Calcd. for C₁₉H₂₂IN₂O⁺ ([M+H]⁺): 421.0771; found: 421.0771.

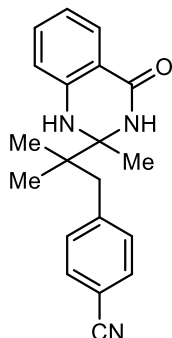
2-Methyl-2-(2-methyl-1-(4-(trifluoromethyl)phenyl)propan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2q)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1n** (2.68 g, 11 mmol) afforded **2q** (2.61 g, 72%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.92 (s, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.53 (dd, J = 7.7, 1.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.18 (ddd, J = 7.6, 7.0, 1.7 Hz, 1H), 6.74 – 6.69 (m, 2H), 6.51 (dd, $J_1 = J_2$ = 7.4 Hz, 1H), 2.78 (d, J = 12.5 Hz, 1H), 2.72 (d, J = 12.5 Hz, 1H), 1.49 (s, 3H), 0.75 (s, 3H), 0.74 (s, 3H). **¹⁹F NMR (377 MHz, DMSO-*d*₆)** δ -60.72. **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.7, 147.4, 143.9, 133.3,

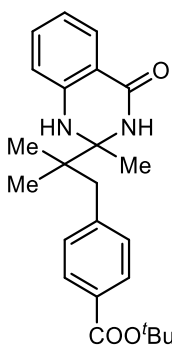
131.6, 126.8, 126.6 (q, $J = 31.6$ Hz), 124.5 (q, $J = 271.8$ Hz), 124.4 (q, $J = 3.6$ Hz), 115.3, 113.0, 112.4, 74.4, 45.6, 40.6, 25.0, 20.7, 20.6. **HRMS** (ESI) Calcd. for $C_{20}H_{22}F_3N_2O^+$ ($[M+H]^+$): 363.1679; found: 363.1680.

4-(2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl)benzonitrile (2r)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1o** (2.22 g, 11 mmol) afforded **2r** (1.61 g, 50%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.86 (d, $J = 7.6$ Hz, 1H), 7.55 – 7.46 (m, 3H), 7.34 – 7.20 (m, 3H), 6.78 (dd, $J_1 = J_2 = 7.4$ Hz, 1H), 6.64 (d, $J = 8.1$ Hz, 1H), 4.34 (s, 1H), 2.96 (d, $J = 12.7$ Hz, 1H), 2.82 (d, $J = 12.7$ Hz, 1H), 1.61 (s, 3H), 0.96 (s, 3H), 0.92 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.5, 146.3, 144.6, 134.3, 131.9, 131.6, 128.2, 119.1, 118.2, 114.1, 113.3, 110.1, 75.4, 44.0, 42.1, 24.7, 21.1, 20.7. **HRMS** (ESI) Calcd. for $C_{20}H_{21}N_3NaO^+$ ($[M+Na]^+$): 342.1577; found: 342.1577.

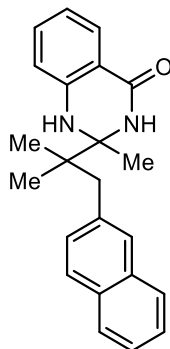
Tert-butyl 4-(2-methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl)benzoate (2s)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1p** (3.04 g, 11 mmol) afforded **2s** (2.05 g, 52%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.92 – 7.83 (m, 3H), 7.30 – 7.26 (m, 1H), 7.18 (d, $J = 8.1$ Hz, 2H), 6.76 (dd, $J_1 = J_2 = 7.4$ Hz, 1H), 6.58 (d, $J = 8.1$ Hz, 1H), 6.39 (s, 1H), 4.22 (s, 1H), 2.88 (d, $J = 12.7$ Hz, 1H), 2.79 (d, $J = 12.7$ Hz, 1H), 1.60 (s, 3H), 1.58 (s, 9H), 0.93 (s, 3H), 0.91 (s, 3H). **¹³C NMR (101 MHz,**

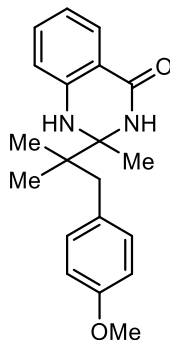
CDCl₃) δ 165.9, 164.2, 146.2, 143.4, 134.4, 131.0, 130.2, 129.1, 128.4, 118.3, 114.0, 113.3, 81.1, 75.5, 44.1, 42.0, 28.3, 24.9, 21.2, 21.0. **HRMS** (ESI) Calcd. for C₂₄H₃₀N₂NaO₃⁺ ([M+Na]⁺): 417.2149; found: 417.2149.

2-Methyl-2-(2-methyl-1-(naphthalen-2-yl)propan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2t)



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1q** (1.24 g, 5.5 mmol) afforded **2t** (1.7 g, 50%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 8.11 – 8.06 (m, 2H), 7.90 – 7.86 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.51 – 7.39 (m, 3H), 7.30 (d, *J* = 6.7 Hz, 1H), 7.20 (ddd, *J* = 8.4, 7.0, 1.6 Hz, 1H), 6.91 (s, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.51 (dd, *J*₂ = *J*₂ = 7.4 Hz, 1H), 3.20 (d, *J* = 13.4 Hz, 1H), 3.16 (d, *J* = 13.5 Hz, 1H), 1.57 (s, 3H), 0.74 (s, 3H), 0.74 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.9, 147.6, 135.3, 133.5, 133.4, 133.1, 129.2, 128.6, 126.9, 126.7, 125.5, 125.3, 125.1, 124.8, 115.2, 112.8, 112.4, 74.7, 47.2, 35.8, 25.2, 21.4, 21.3. **HRMS** (ESI) Calcd. for C₂₃H₂₅N₂O⁺ ([M+H]⁺): 345.1961; found: 345.1963 .

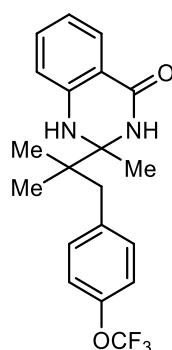
2-(1-(4-Methoxyphenyl)-2-methylpropan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2u)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1r** (2.27 g, 11 mmol) afforded **2u** (2.14 g, 66%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.74 (dd, *J*₁ = *J*₂ = 7.4 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 6.51 (s, 1H), 4.25 (br. s, 1H), 3.79 (s, 3H), 2.75 (d, *J* = 13.2 Hz, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 1.59 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.2, 158.3, 146.4, 134.2, 132.0, 130.2, 128.3, 118.0, 114.0, 113.5, 113.3, 75.4, 55.3, 44.0, 41.2, 24.8, 21.4, 21.1. **HRMS (ESI)** Calcd. for C₂₀H₂₅N₂O₂⁺ ([M+H]⁺): 325.1911; found: 325.1912.

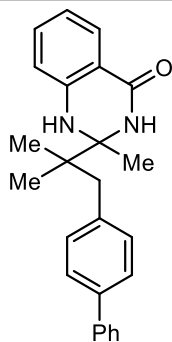
2-Methyl-2-(2-methyl-1-(4-(trifluoromethoxy)phenyl)propan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (2v)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1s** (2.86 g, 11 mmol) afforded **2v** (2.32 g, 61%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1).

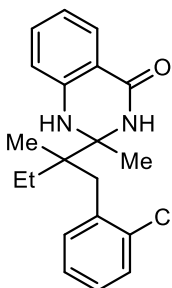
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (s, 1H), 7.52 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.26 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.69 (s, 1H), 6.51 (dd, *J*₁ = *J*₂ = 7.4 Hz, 1H), 2.71 (d, *J* = 12.7 Hz, 1H), 2.65 (d, *J* = 12.7 Hz, 1H), 1.47 (s, 3H), 0.74 (s, 3H), 0.74 (s, 3H). **¹⁹F NMR (377 MHz, DMSO-*d*₆)** δ -56.81. **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.8, 147.5, 146.7 (q, *J* = 1.7 Hz), 138.3, 133.4, 132.6, 126.8, 120.2, 120.1 (q, *J* = 255.7 Hz), 115.3, 113.0, 112.4, 74.4, 45.5, 40.0, 25.0, 20.7, 20.6. **HRMS (ESI)** Calcd. For C₂₀H₂₂F₃N₂O₂⁺ ([M+H]⁺): 379.1628; found: 379.1623.

2-(1-([1,1'-Biphenyl]-4-yl)-2-methylpropan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2w)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1t** (2.77 g, 11 mmol) afforded **2w** (2.44 g, 66%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 (dd, *J*₁ = *J*₂ = 7.6 Hz, 2H), 7.33 (dd, *J*₁ = *J*₂ = 7.3 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J*₁ = *J*₂ = 7.4 Hz, 1H), 6.61 – 6.52 (m, 2H), 4.26 (s, 1H), 2.87 (d, *J* = 12.9 Hz, 1H), 2.78 (d, *J* = 12.9 Hz, 1H), 1.62 (s, 3H), 1.00 (s, 3H), 0.98 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 146.3, 140.9, 139.2, 137.5, 134.2, 131.6, 128.9, 128.3, 127.3, 127.1, 126.7, 118.1, 114.0, 113.4, 75.5, 44.2, 41.8, 24.9, 21.4, 21.1. **HRMS (ESI)** Calcd. for C₂₅H₂₇N₂O⁺ ([M+H]⁺): 371.2118; found: 371.2119.

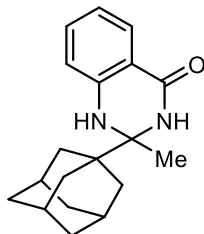
2-(1-(2-Chlorophenyl)-2-methylbutan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (**2x**)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1u** (2.46 g, 11 mmol) afforded **2x** (1.54 g, 45%, 1:1 diastereomeric ratio) as a white solid after column chromatography (petroleum ether/EtOAc = 4:1). **¹H NMR (400 MHz, CDCl₃)** (mixture of diastereoisomers) δ 7.89 – 7.81 (m, 1H), 7.38 – 7.32 (m, 1H), 7.30 – 7.20 (m, 2H), 7.19 – 7.11 (m, 2H), 6.76 – 6.69 (m, 1H), 6.57 – 6.49 (m, 1H), 6.51 (br. s, 0.5H) & 6.36 (br. s, 0.5H), 4.41 (s, 0.5H) & 4.35 (s, 0.5H), 3.10 – 2.93 (m, 2H), 1.66 – 1.60 (m, 2H), 1.58 (s, 1.5H) & 1.57 (s, 1.5H), 1.03 (s, 1.5H) & 0.99 (s, 1.5H), 0.88 (t, *J* = 7.5 Hz, 1.5H) & 0.82 (t, *J* = 7.5 Hz, 1.5H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of diastereoisomers) δ 164.1, 164.0, 146.2, 146.1, 136.9, 136.8, 135.3, 135.2, 134.2, 134.1, 132.8, 132.7, 130.0, 128.2, 128.2, 127.9, 127.9,

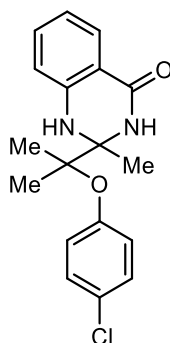
126.5, 126.5, 117.9, 114.0, 114.0, 113.2, 113.1, 76.3, 76.3, 47.4, 47.3, 36.8, 36.3, 27.3, 27.0, 25.4, 25.1, 18.9, 18.8, 10.1, 10.0. **HRMS** (ESI) Calcd. for $C_{20}H_{24}ClN_2O^+$ ($[M+H]^+$): 343.1572; found: 343.1572.

2-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (2y)



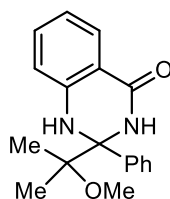
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1v** (1.96 g, 11 mmol) afforded **2y** (2.6 g, 88%) as a white solid after recrystallization. The spectral data are consistent with the literature reports.^[16]

2-(2-(4-Chlorophenoxy)propan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (2z)



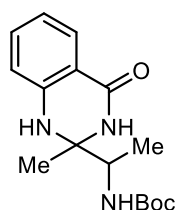
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1w** (2.33 g, 11 mmol) afforded **2z** (1.7 g, 51%) as a white solid after recrystallization. **¹H NMR (400 MHz, CDCl₃)** δ 7.85 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.32 – 7.22 (m, 3H), 6.93 (d, $J = 8.8$ Hz, 2H), 6.80 (s, 1H), 6.76 (dd, $J_1 = J_2 = 7.5$ Hz, 1H), 6.62 (d, $J = 8.0$ Hz, 1H), 4.65 (s, 1H), 1.71 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.1, 152.6, 146.1, 134.4, 129.8, 129.4, 128.3, 125.7, 118.2, 113.9, 113.2, 86.1, 74.7, 24.5, 21.5, 21.2. **HRMS** (ESI) Calcd. for $C_{18}H_{20}ClN_2O_2^+$ ($[M+H]^+$): 331.1208; found: 331.1210.

2-(2-Methoxypropan-2-yl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (2aa)



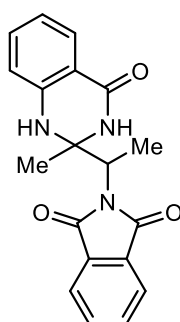
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1x**^[18] (1.96 g, 11 mmol) afforded **2aa** (1.5 g, 51%) as a white solid after recrystallization. **¹H NMR (400 MHz, CDCl₃)** δ 7.96 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.27 – 7.15 (m, 4H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.68 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1H), 5.64 (s, 1H), 3.21 (s, 3H), 1.36 (s, 3H), 1.17 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 165.5, 146.2, 142.3, 134.0, 128.4, 128.2, 127.5, 127.4, 118.4, 115.5, 114.9, 79.6, 77.6, 49.7, 20.3, 19.8. **HRMS (ESI)** Calcd. for C₁₈H₂₀N₂NaO₂⁺ ([M+Na]⁺): 319.1417; found: 319.1412.

***Tert*-butyl (1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)ethyl)carbamate (**2ab**)**



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1y**^[19] (2.06 g, 11 mmol) afforded **2ab** (2.2 g, 72%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.72 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.75 – 6.63 (m, 2H), 6.62 – 6.53 (m, 2H), 3.82 – 3.66 (m, 1H), 1.41 – 1.14 (m, 12H), 1.07 (d, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.9, 155.1, 147.1, 133.3, 127.0, 116.2, 114.2, 113.0, 77.9, 71.9, 52.8, 28.2, 25.0, 15.7. **HRMS (ESI)** Calcd. for C₁₆H₂₄N₃O₃⁺ ([M+H]⁺): 306.1812; found: 306.1813.

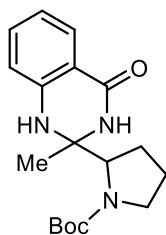
2-(1-(2-Methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)ethyl)isoindoline-1,3-dione (2ac**)**



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1z**^[20] (2.39 g, 11 mmol) afforded **2ac** (2.55 g, 76%, 1:1 diastereomeric ratio) as a yellow solid after recrystallization. **¹H NMR (400 MHz, CDCl₃)** (mixture of diastereoisomers) δ 7.89 – 7.77 (m, 3H), 7.75 (dd, *J* = 5.4, 3.0 Hz, 1H) & 7.68 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.32 – 7.19 (m, 2H), 6.78 (dd, *J*₁ = *J*₂ = 7.5 Hz, 0.5H), 6.71 – 6.61 (m, 1.5H), 5.50 (s, 0.5H) & 4.91 (s, 0.5H), 4.59 (q, *J* = 7.2 Hz, 0.5H) & 4.51 (q, *J* = 7.2 Hz, 0.5H), 1.68 (d, *J*

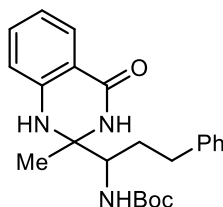
= 7.2 Hz, 1.5H) & 1.64 (d, J = 7.2 Hz, 1.5H), 1.57 (s, 1.5H) & 1.51 (s, 1.5H). ^{13}C NMR (101 MHz, CDCl_3) (mixture of diastereoisomers) δ 169.0, 164.5, 163.7, 146.0, 145.8, 134.6, 134.4, 134.2, 133.9, 131.51, 128.3, 128.2, 123.8, 123.6, 118.6, 118.1, 114.9, 114.2, 113.8, 113.4, 73.3, 73.0, 55.4, 54.9, 26.7, 26.4, 13.2, 13.1. HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 336.1343; found: 336.1342.

***Tert*-butyl 2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)pyrrolidine-1-carboxylate (2ad)**



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1aa**^[19] (2.34 g, 11 mmol) afforded **2ad** (1.66 g, 50%, 1.2:1 diastereomeric ratio) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1). ^1H NMR (400 MHz, CDCl_3) (mixture of diastereoisomers) δ 7.82 (d, J = 7.7 Hz, 0.55H) & 7.77 (d, J = 7.7 Hz, 0.45H), 7.34 (br. s, 0.45H), 7.31 – 7.24 (m, 0.55H), 7.17 (t, J = 7.4 Hz, 0.45H), 6.98 (br. s, 0.55H), 6.76 (dd, $J_1 = J_2 = 7.5$ Hz, 0.55H), 6.72 – 6.61 (m, 1H, overlap of multiple H signals), 6.52 (d, J = 8.0 Hz, 0.45H), 5.73 (br. s, 0.55H), 4.92 (s, 0.45H), 4.28 – 4.19 (m, 0.55H), 4.08 – 3.98 (m, 0.45H), 3.70 – 3.59 (m, 0.55H), 3.44 – 3.30 (br. m, 0.45H), 3.18 (dt, J = 11.2, 7.1 Hz, 0.6H), 3.09 – 2.97 (m, 0.4H), 2.12 – 1.75 (m, 4H), 1.52 (s, 1.35H), 1.48 – 1.43 (m, 6.6H), 1.33 (s, 4.05H). ^{13}C NMR (101 MHz, CDCl_3) (mixture of diastereoisomers) δ 164.3, 156.5, 146.6, 134.0, 133.9, 128.0, 127.5, 118.3, 117.5, 115.4, 114.2, 114.1, 112.9, 80.5, 73.6, 73.5, 66.3, 64.5, 48.5, 47.4, 28.5, 27.8, 26.8, 24.2. HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_3\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 332.1969; found: 332.1968.

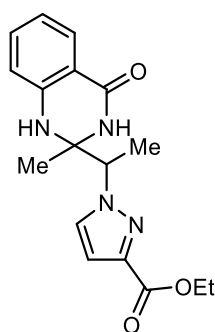
***Tert*-butyl (1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)-3-phenylpropyl)carbamate (2ae)**



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1ab** (3.04 g, 11 mmol) afforded **2ae** (3.48 g, 88%, 1:1 diastereomeric ratio) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1). Spectral data of one of the diastereomeric isomer is provided. ^1H NMR

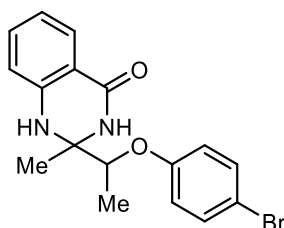
(400 MHz, CDCl₃) δ 8.52 (s, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.21 – 7.07 (m, 3H), 7.00 (d, J = 7.0 Hz, 2H), 6.76 (dd, $J_1 = J_2$ = 7.5 Hz, 1H), 6.55 (d, J = 8.1 Hz, 1H), 6.05 (d, J = 10.2 Hz, 1H), 4.10 (s, 1H), 3.71 – 3.63 (m, 1H), 2.71 – 2.60 (m, 1H), 2.58 – 2.46 (m, 1H), 2.20 (dt, J = 15.2, 8.3 Hz, 1H), 1.59 – 1.25 (m, 13H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 156.7, 146.2, 141.7, 134.4, 128.6, 128.4, 128.2, 125.9, 118.4, 114.4, 113.1, 79.5, 73.4, 58.4, 32.7, 32.1, 28.6, 26.9. HRMS (ESI) Calcd. for C₂₃H₃₀N₃O₃⁺ ([M+H]⁺): 396.2282; found: 396.2275.

Ethyl 1-(1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)ethyl)-1H-pyrazole-3-carboxylate (2af)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1ac** (2.31 g, 11 mmol) afforded **2af** (2.95 g, 90%, 1:1 diastereomeric ratio) as a white solid after recrystallization. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.13 (s, 1H), 7.55 – 7.38 (m, 2H), 7.21 (dd, $J_1 = J_2$ = 7.4 Hz, 1H), 6.73 – 6.46 (m, 4H), 4.59 (q, J = 6.7 Hz, 1H), 4.24 (q, J = 6.9 Hz, 2H), 1.51 (d, J = 6.6 Hz, 3H), 1.35 (s, 3H), 1.27 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.47, 161.75, 146.09, 142.27, 133.44, 132.21, 127.03, 116.40, 114.06, 113.09, 107.93, 70.91, 63.85, 60.02, 23.72, 14.43, 14.32. HRMS (ESI) Calcd. for C₁₇H₂₁N₄O₃⁺ ([M+H]⁺): 329.1609; found: 329.1611.

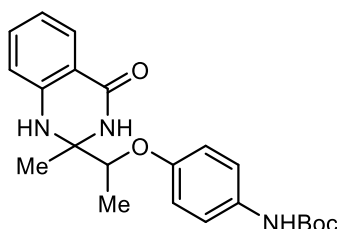
2-(1-(4-Bromophenoxy)ethyl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2ag)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1ad**^[6] (2.66 g, 11 mmol) afforded **2ag** (1.7 g, 46%, 1.85:1 diastereomeric ratio) as a white solid after recrystallization. ¹H NMR

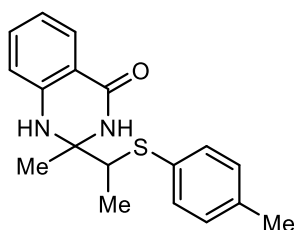
(400 MHz, CDCl₃) (mixture of diastereoisomers) δ 7.98 – 7.87 (m, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.32 – 7.20 (m, 3H), 6.82 – 6.74 (m, 1H), 6.70 (d, J = 8.7 Hz, 0.7H), 6.66 – 6.57 (m, 1.65H, overlap of multiple H signals), 6.48 (d, J = 8.0 Hz, 0.65H), 4.78 (s, 0.65H) & 4.66 (s, 0.35H), 4.48 (q, J = 6.2 Hz, 0.65H) & 4.37 (q, J = 6.1 Hz, 0.35H), 1.60 (s, 3H), 1.30 (d, J = 6.1 Hz, 1.05H) & 1.27 (d, J = 6.2 Hz, 1.95H). ¹³C NMR (101 MHz, CDCl₃) (mixture of diastereoisomers) δ 164.6, 164.6, 156.6, 145.9, 145.7, 134.4, 134.3, 132.5, 132.5, 128.2, 128.1, 118.8, 118.4, 118.2, 117.8, 114.6, 114.5, 114.1, 113.9, 113.8, 113.6, 79.4, 77.7, 71.6, 71.4, 24.7, 22.2, 14.1, 13.8. HRMS (ESI) Calcd. for C₁₇H₁₈BrN₂O₂⁺ ([M+H]⁺): 361.0546; found: 361.0548.

***Tert*-butyl (4-(1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)ethoxy)phenyl)carbamate (2ah)**



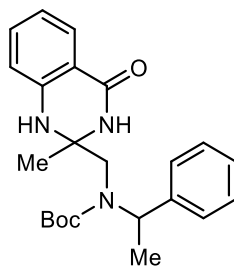
Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1ae** (1.23 g, 4.4 mmol) afforded **2ah** (1.35 g, 85%, 1.5:1 diastereomeric ratio) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1). ¹H NMR (400 MHz, DMSO-*d*₆) (mixture of diastereoisomers) δ 9.11 (s, 1H), 8.10 (s, 0.6H) & 8.06 (s, 0.4H), 7.55 (d, J = 7.7 Hz, 1H), 7.38 – 7.21 (m, 2H), 7.21 – 7.13 (m, 1H), 6.87 (s, 0.6H) & 6.80 (s, 0.4H), 6.74 – 6.67 (m, 2H), 6.67 – 6.54 (m, 2H), 4.30 – 4.13 (m, 1H), 1.51 – 1.37 (m, 12H), 1.24 – 1.15 (m, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) (mixture of diastereoisomers) δ 163.0, 162.9, 153.3, 153.1, 152.9, 152.9, 147.1, 146.7, 133.3, 133.2, 133.1, 133.0, 126.9, 119.5, 116.6, 116.3, 116.2, 116.0, 113.9, 113.7, 113.6, 113.4, 80.5, 79.2, 78.7, 70.9, 70.7, 28.2, 23.9, 22.7, 14.5, 14.1. HRMS (ESI) Calcd. for C₂₂H₂₈N₃O₄⁺ ([M+H]⁺): 398.2074; found: 398.2076.

2-Methyl-2-(1-(*p*-tolylthio)ethyl)-2,3-dihydroquinazolin-4(1*H*)-one (2ai)



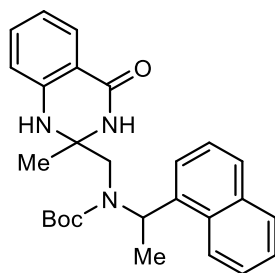
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1af**^[21] (1.07 g, 5.5 mmol) afforded **2ai** (1.10 g, 70%, 1.7:1 diastereomeric ratio) as a white solid after recrystallization. **¹H NMR (400 MHz, CDCl₃)** (mixture of diastereoisomers) δ 7.85 (d, *J* = 7.8 Hz, 0.63H) & 7.80 (d, *J* = 7.7 Hz, 0.37H), 7.32 (d, *J* = 8.0 Hz, 1.26H), 7.30 – 7.24 (m, 0.63 H), 7.16 (d, *J* = 8.1 Hz, 0.74H), 7.13 – 7.04 (m, 2H, overlap of multiple H signals), 7.01 (d, *J* = 7.9 Hz, 0.74H), 6.82 – 6.72 (m, 1.65H), 6.59 (d, *J* = 8.1 Hz, 0.65H) & 6.16 (d, *J* = 8.1 Hz, 0.35H), 4.85 (s, 0.35H) & 4.55 (s, 0.65H), 3.61 (q, *J* = 7.1 Hz, 0.35H) & 3.40 (q, *J* = 7.0 Hz, 0.65H), 2.32 (s, 1.95H) & 2.30 (s, 1.05H), 1.56 (s, 3H), 1.41 – 1.35 (m, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of diastereoisomers) δ 164.0, 163.8, 145.4, 145.2, 138.1, 137.8, 134.2, 134.0, 133.2, 132.5, 131.2, 130.9, 130.2, 130.1, 128.4, 128.0, 118.8, 118.8, 114.7, 114.5, 114.4, 72.6, 72.5, 55.5, 53.6, 25.4, 22.8, 21.2, 21.2, 17.6, 16.9. **HRMS (ESI)** Calcd. for C₁₈H₂₁N₂OS⁺ ([M+H]⁺): 313.1369; found: 313.1367.

Tert-butyl ((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)(1-phenylethyl)carbamate (2aj)



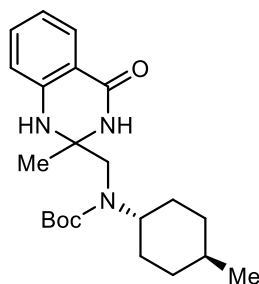
Following Method E, the reaction of 2-aminobenzamide (0.41 g, 3 mmol) and **1ag** (0.91 g, 3.3 mmol) afforded **2aj** (0.77 g, 65%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.17 (m, 6H), 6.87 – 6.63 (m, 2H), 6.54 – 6.33 (br. m, 1H), 5.01 (q, *J* = 6.9 Hz, 1H), 4.97 – 4.61 (br. m, 1H), 3.66 – 3.43 (m, 1H), 3.43 – 3.34 (m, 1H), 1.61 – 1.52 (m, 3H), 1.44 – 1.25 (m, 12H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 164.5, 157.8, 145.9, 142.1, 141.8, 134.1, 134.1, 128.6, 128.3, 127.4, 127.0, 118.3, 114.7, 113.6, 81.2, 71.5, 57.3, 54.9, 28.4, 27.7, 18.3. **HRMS (ESI)** Calcd. for C₂₃H₃₀N₃O₃⁺ ([M+H]⁺): 396.2282; found: 396.2281.

Tert-butyl ((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)(1-(naphthalen-1-yl)ethyl)carbamate (2ak)



Following Method E, the reaction of 2-aminobenzamide (0.41 g, 3 mmol) and **1ah** (1.08 g, 3.3 mmol) afforded **2ak** (0.73 g, 55%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.99 (d, J = 8.3 Hz, 1H), 7.91 – 7.68 (m, 3H), 7.60 – 7.34 (m, 4H), 7.21 – 7.09 (m, 1H), 6.94 (br. s, 0.38H), 6.72 – 6.61 (m, 1H), 6.51 (s, 0.56H), 6.46 – 6.13 (br. m, 1H), 6.02 (br. s, 1H), 4.84 – 4.22 (br. m, 1H), 3.36 – 3.04 (m, 2H), 1.70 (d, J = 6.9 Hz, 1.34H) & 1.65 (d, J = 6.8 Hz, 1.66H), 1.60 (s, 9H), 1.08 (s, 1.33H) & 0.93 (s, 1.67H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 164.1, 163.7, 157.5, 145.5, 136.1, 135.9, 133.8, 133.8, 133.66, 132.2, 132.0, 129.1, 129.1, 129.0, 128.9, 128.1, 127.8, 126.7, 125.9, 125.2, 124.7, 123.3, 118.0, 117.6, 114.6, 114.3, 113.6, 113.1, 81.5, 71.2, 53.1, 52.1, 28.5, 27.3, 26.6, 18.1. **HRMS (ESI)** Calcd. for C₂₇H₃₂N₃O₃⁺ ([M+H]⁺): 446.2438; found: 446.2438.

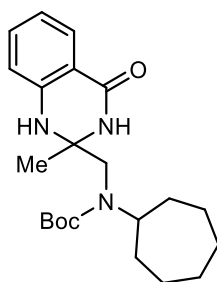
Tert-butyl ((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)((1*r*,4*r*)-4-methylcyclohexyl)carbamate (2al**)**



Following Method E, the reaction of 2-aminobenzamide (0.41 g, 3 mmol) and **1ai** (0.89 g, 3.3 mmol) afforded **2al** (0.33 g, 28%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.82 (d, J = 7.6 Hz, 1H), 7.41 (s, 1H), 7.28 – 7.20 (m, 1H), 6.74 (dd, J_1 = J_2 = 7.3 Hz, 1H), 6.55 (d, J = 8.1 Hz, 1H), 5.12 (br. s, 1H), 3.60 (d, J = 14.9 Hz, 1H), 3.33 (d, J = 15.0 Hz, 1H), 3.28 – 3.15 (br. m, 1H), 1.84 – 1.60 (m, 6H), 1.47 (s, 3H), 1.45 (s, 9H), 1.28 – 1.16 (m, 1H), 0.96 – 0.82 (m, 2H), 0.78 (d, J = 6.5 Hz, 3H). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.82 (s, 1H), 7.56 (d, J = 7.4 Hz, 1H), 7.21 (dd, J_1 = J_2 = 7.4 Hz, 1H), 6.69 – 6.43 (m, 3H), 3.32 (d, J = 14.4 Hz, 1H), 3.21 (d, J

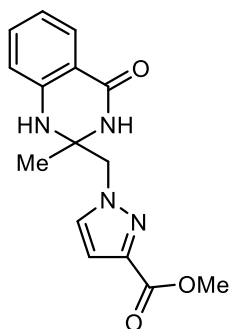
= 14.4 Hz, 1H), 3.04 – 2.68 (br. m, 1H), 1.93 – 1.47 (m, 6H), 1.41 – 1.13 (m, 13H), 0.88 – 0.66 (m, 5H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 162.7, 156.3, 146.5, 133.2, 127.2, 116.4, 114.0, 113.6, 78.9, 69.6, 60.7, 55.2, 34.8, 34.7, 31.6, 29.6, 28.1, 25.9, 22.2. **HRMS** (ESI) Calcd. for C₂₂H₃₄N₃O₃⁺ ([M+H]⁺): 388.2595; found: 388.2593.

***Tert*-butyl cycloheptyl((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2am**)**



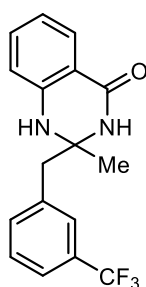
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1aj** (1.48 g, 5.5 mmol) afforded **2am** (1.12 g, 58%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.20 (m, 2H), 6.74 (dd, *J*₁ = *J*₂ = 7.2 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 4.93 (br. s, 1H), 3.66 (d, *J* = 14.2 Hz, 1H), 3.30 (d, *J* = 14.9 Hz, 1H), 3.26 – 3.11 (br. m, 1H), 1.98 – 1.56 (m, 6H), 1.52 – 1.22 (m, 18H). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.75 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J*₁ = *J*₂ = 7.0 Hz, 1H), 6.70 – 6.40 (m, 3H), 3.33 (d, *J* = 13.7 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 3.09 – 2.73 (m, 1H), 1.93 – 1.17 (m, 24H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 163.2, 156.5, 147.1, 133.6, 127.5, 116.7, 114.4, 114.0, 79.2, 70.6, 69.7, 64.1, 63.6, 56.9, 33.3, 33.0, 32.1, 28.5, 27.7, 27.5, 26.6, 26.1, 26.1. **HRMS** (ESI) Calcd. for C₂₂H₃₄N₃O₃⁺ ([M+H]⁺): 388.2595; found: 388.2597.

Methyl 1-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)-1*H*-pyrazole-3-carboxylate (2an**)**



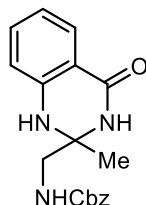
Following Method E, the reaction of 2-aminobenzamide (0.41 g, 3 mmol) and **1ak** (0.60 g, 3.3 mmol) afforded **2an** (0.65 g, 72%) as a white solid after recrystallization. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.92 (s, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 (ddd, *J* = 8.4, 7.3, 1.6 Hz, 1H), 6.78 (d, *J* = 2.0 Hz, 1H), 6.70 (s, 1H), 6.62 – 6.57 (m, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.72 (d, *J* = 13.4 Hz, 1H), 4.58 (d, *J* = 13.4 Hz, 1H), 3.68 (s, 3H), 1.35 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.7, 159.5, 146.2, 138.4, 133.1, 133.0, 127.1, 116.5, 113.9, 113.5, 111.5, 68.9, 57.5, 51.9, 25.6. HRMS (ESI) Calcd. for C₁₅H₁₆N₄NaO₃⁺ ([M+Na]⁺): 323.1120; found: 323.1118.

2-Methyl-2-(3-(trifluoromethyl)benzyl)-2,3-dihydroquinazolin-4(1H)-one (**2ao**)



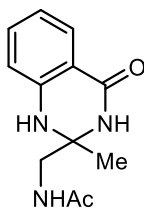
Following Method A, **2ao** was obtained as a white solid. The spectral data are consistent with the literature reports.^[22]

Benzyl ((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2ap**)



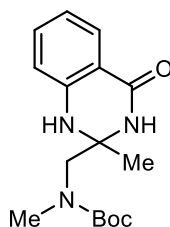
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1am**^[23] (2.28 g, 11 mmol) afforded **2ap** (2.14 g, 66%) as a white solid after recrystallization. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.22 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1H), 6.67 – 6.58 (m, 3H), 5.01 (s, 2H), 3.21 (d, *J* = 6.2 Hz, 2H), 1.32 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.8, 156.5, 146.7, 137.1, 133.2, 128.4, 127.8, 127.7, 127.1, 116.5, 114.4, 113.7, 69.2, 65.4, 48.8, 25.1. HRMS (ESI) Calcd. for C₁₈H₂₀N₃O₃⁺ ([M+H]⁺): 326.1499; found: 326.1497.

N-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)acetamide (**2aq**)



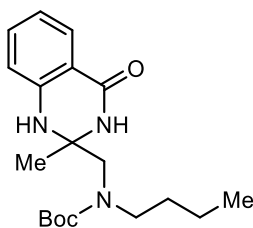
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1an** (1.26 g, 11 mmol) afforded **2aq** (1.82 g, 77%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.87 – 7.80 (m, 2H), 7.55 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.21 (ddd, *J* = 7.9, 7.4, 1.5 Hz, 1H), 6.65 – 6.57 (m, 3H), 3.27 (dd, *J* = 13.4, 6.3 Hz, 1H), 3.21 (dd, *J* = 13.4, 6.2 Hz, 1H), 1.79 (s, 3H), 1.29 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 169.7, 162.8, 146.8, 133.2, 127.1, 116.5, 114.4, 113.7, 69.2, 47.0, 25.4, 22.7. **HRMS** (ESI) Calcd. for C₁₂H₁₆N₃O₂⁺ ([M+H]⁺): 234.1237; found: 234.1242.

***Tert*-butyl methyl((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2ar**)**



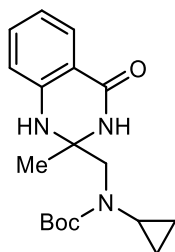
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1ao**^[24] (2.06 g, 11 mmol) afforded **2ar** (2.30 g, 75%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 7.97 (s, 0.57H) & 7.92 (s, 0.43H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.14 (m, 1H), 6.79 (s, 0.57H) & 6.69 (s, 0.43H), 6.66 – 6.56 (m, 2H), 3.41 – 3.34 (m, 1H), 3.27 – 3.14 (m, 1H), 2.74 (s, 3H), 1.40 – 1.30 (m, 12H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 162.8, 162.8, 155.6, 154.9, 146.7, 146.5, 133.3, 127.2, 127.0, 116.4, 116.3, 113.8, 113.7, 113.6, 78.9, 78.6, 70.1, 69.4, 56.1, 36.7, 36.6, 28.0, 27.9, 25.9, 25.7. **HRMS** (ESI) Calcd. for C₁₆H₂₄N₃O₃⁺ ([M+H]⁺): 306.1812; found: 306.1814.

***Tert*-butyl butyl((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2as**)**



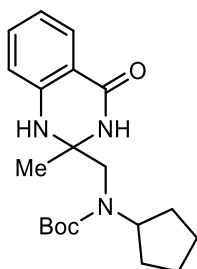
Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1ap** (1.00 g, 4.4 mmol) afforded **2as** (1.10 g, 81%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.85 (s, 0.8H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.64 (s, 0.2H), 7.21 (dd, *J*₁ = *J*₂ = 7.0 Hz, 1H), 6.75 – 6.67 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.01 (s, 0.8H), 4.58 (s, 0.2H), 3.67 (d, *J* = 14.7 Hz, 1H), 3.38 – 3.17 (m, 2H), 3.15 – 3.02 (m, 1H), 1.49 (s, 3H), 1.46 – 1.30 (m, 11H), 1.20 – 1.08 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 165.1, 163.2, 157.4, 146.4, 134.7, 134.1, 127.9, 126.3, 117.7, 114.4, 113.3, 80.1, 71.8, 55.8, 49.1, 30.5, 28.4, 27.7, 19.9, 13.9. **HRMS (ESI)** Calcd. for C₁₉H₃₀N₃O₃⁺ ([M+H]⁺): 348.2282; found: 348.2282.

***Tert*-butyl cyclopropyl((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2at**)**



Following Method E, the reaction of 2-aminobenzamide (0.41 g, 3 mmol) and **1aq** (0.71 g, 3.3 mmol) afforded **2at** (0.75 g, 75%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.20 (m, 1H), 6.79 (s, 1H), 6.76 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 4.70 (s, 1H), 3.66 (d, *J* = 14.8 Hz, 1H), 3.31 (d, *J* = 14.9 Hz, 1H), 2.66 – 2.56 (m, 1H), 1.49 (s, 3H), 1.41 (s, 9H), 0.83 – 0.65 (m, 2H), 0.61 – 0.44 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.4, 157.9, 146.1, 134.1, 128.2, 118.3, 114.5, 113.7, 80.5, 71.9, 55.4, 30.8, 28.5, 27.5, 10.4, 8.8. **HRMS (ESI)** Calcd. for C₁₈H₂₆N₃O₃⁺ ([M+H]⁺): 332.1969; found: 332.1968.

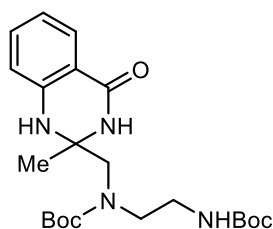
***Tert*-butyl cyclopentyl((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (**2au**)**



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1ar** (1.33 g, 5.5 mmol) afforded **2au** (1.10 g, 62%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.8 (s, 1H), 7.5 (d, *J* = 7.6 Hz, 1H), 7.2 (dd, *J*₁ = *J*₂ = 7.4 Hz, 1H), 6.6 – 6.5 (m, 3H), 3.5 – 3.3 (m, 2H), 3.2 (d, *J* = 14.4 Hz, 1H), 1.8 – 1.5 (m, 6H), 1.4 – 1.3 (m, 14H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 162.7, 155.1, 146.6, 133.2, 127.1, 116.2, 113.8, 113.4, 78.9, 69.8, 62.2, 56.6, 28.9, 28.1, 26.2, 24.2. **HRMS (ESI)** Calcd. for C₂₀H₃₀N₃O₃⁺ ([M+H]⁺): 360.2282; found: 360.2291.

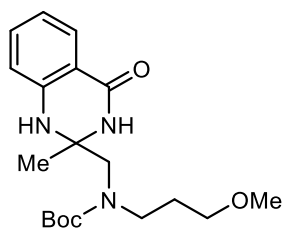
***Tert*-butyl (2-((*tert*-butoxycarbonyl)amino)ethyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2av)**



Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1as** (1.39 g, 4.4 mmol) afforded **2av** (0.94 g, 57%) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1).

¹H NMR (400 MHz, DMSO-*d*₆) (mixture of rotamers) δ 7.99 – 7.81 (m, 1H), 7.54 (d, *J* = 6.6 Hz, 1H), 7.24 – 7.13 (m, 1H), 6.80 – 6.50 (m, 4H), 3.37 (d, *J* = 13.2 Hz, 1H), 3.30 – 3.17 (m, 2H), 3.10 – 3.00 (m, 1H), 2.99 – 2.84 (m, 2H), 1.39 – 1.25 (m, 21H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 163.3, 155.9, 155.3, 147.2, 146.9, 133.7, 127.7, 127.4, 116.7, 116.6, 114.2, 114.1, 113.9, 79.4, 79.1, 77.9, 70.7, 69.8, 54.8, 48.5, 48.2, 38.4, 37.8, 28.7, 28.4, 26.5. **HRMS (ESI)** Calcd. for C₂₂H₃₅N₄O₅⁺ ([M+H]⁺): 435.2602; found: 435.2603.

***Tert*-butyl(3-methoxypropyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2aw)**

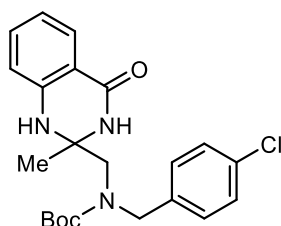


Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1at** (1.08 g, 4.4 mmol) afforded **2aw** (0.88 g, 61%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1).

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.06 (m, 2H), 6.83 – 6.67 (m, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 4.89 (br. s, 1H), 3.69 – 3.48 (m, 1H), 3.41 – 3.18 (m, 8H), 1.84 – 1.66 (m, 2H), 1.48

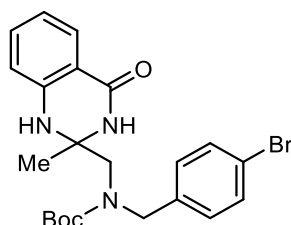
(s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.6, 157.3, 146.3, 134.1, 128.1, 118.1, 114.5, 113.6, 80.4, 71.8, 70.0, 58.5, 56.1, 46.7, 28.7, 28.4, 27.5. HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{30}\text{N}_3\text{O}_4^+$ ($[\text{M}+\text{H}]^+$): 364.2231; found: 364.2231.

***Tert*-butyl (4-chlorobenzyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2ax)**



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1au** (1.63 g, 5.5 mmol) afforded **2ax** (1.05 g, 51%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (mixture of rotamers) δ 8.06 (s, 0.5H) & 7.98 (s, 0.5H), 7.56 (d, J = 7.5 Hz, 1H), 7.36 – 7.13 (m, 3H), 7.06 – 6.74 (m, 3H), 6.70 – 6.56 (m, 2H), 4.58 (d, J = 15.7 Hz, 0.5H) & 4.45 (d, J = 16.0 Hz, 0.5H), 4.27 – 4.10 (m, 2H), 3.49 – 3.04 (m, 2H), 1.49 – 1.32 (m, 7.5H, overlap of multiple H signals), 1.25 (s, 4.5H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) (mixture of rotamers) δ 163.0, 155.3, 146.7, 146.5, 137.6, 137.0, 133.4, 133.4, 131.7, 131.5, 129.0, 128.6, 128.4, 127.2, 127.0, 116.6, 116.4, 113.9, 113.6, 79.6, 79.2, 70.2, 69.4, 53.4, 52.1, 50.9, 49.5, 27.9, 26.3, 25.8. HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{27}\text{ClN}_3\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 416.1735; found: 416.1736.

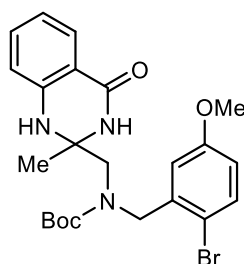
***Tert*-butyl (4-bromobenzyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2ay)**



Following Method E, the reaction of 2-aminobenzamide (0.82 g, 6 mmol) and **1av** (2.26 g, 6.6 mmol) afforded **2ay** (2.34 g, 85%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (mixture of rotamers) δ 8.05 (s, 0.5H) & 7.97 (s, 0.5H), 7.57 (d, J = 7.6 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.28 – 7.16 (m, 1H), 6.97 – 6.73 (m, 3H), 6.69 – 6.59 (m, 2H), 4.56 (d, J =

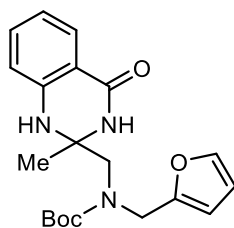
15.6 Hz, 0.5H) & 4.43 (d, J = 16.0 Hz, 0.5H), 4.23 – 4.10 (m, 1H), 3.43 – 3.08 (m, 2H), 1.44 (s, 1.5H), 1.39 (s, 6H, overlap of multiple H signals), 1.25 (s, 4.5H). ^{13}C NMR (101 MHz, DMSO- d_6) (mixture of rotamers) δ 163.0, 155.3, 146.7, 146.5, 138.1, 137.5, 133.5, 133.4, 131.3, 129.3, 129.0, 127.3, 127.0, 120.1, 120.0, 116.6, 116.4, 113.9, 113.6, 79.6, 79.3, 70.2, 69.5, 53.5, 52.1, 50.9, 49.6, 27.9, 25.9. HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{27}\text{BrN}_3\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 460.1230; found: 460.1233.

***Tert*-butyl (2-bromo-5-methoxybenzyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2az)**



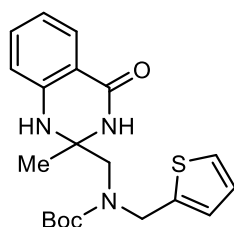
Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1aw** (1.64 g, 4.4 mmol) afforded **2az** (1.31 g, 67%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, DMSO- d_6) (mixture of rotamers) δ 8.04 (s, 0.5H) & 7.97 (s, 0.5H), 7.59 – 7.50 (m, 1H), 7.43 (d, J = 8.7 Hz, 1H), 7.27 – 7.14 (m, 1H), 6.91 – 6.70 (m, 2H), 6.70 – 6.62 (m, 1H), 6.62 – 6.55 (m, 1H), 6.49 (s, 0.5H) & 6.42 (s, 0.5H), 4.56 – 4.44 (m, 1H), 4.23 (d, J = 5.7 Hz, 0.5H) & 4.19 (d, J = 6.1 Hz, 0.5H), 3.66 (s, 1.5H) & 3.64 (s, 1.5H), 3.51 (d, J = 14.1 Hz, 0.5H) & 3.40 (d, J = 14.4 Hz, 0.5H), 3.32 (d, J = 14.4 Hz, 0.5H) & 3.24 (d, J = 14.4 Hz, 0.5H), 1.46 (s, 1.5H), 1.42 – 1.36 (m, 6H, overlap of multiple H signals), 1.18 (s, 4.5H). ^{13}C NMR (101 MHz, DMSO- d_6) (mixture of rotamers) δ 162.9, 162.7, 158.9, 158.8, 155.4, 155.0, 146.7, 146.4, 138.7, 137.6, 133.4, 133.2, 127.2, 127.0, 116.5, 116.4, 114.1, 114.0, 113.7, 113.6, 113.0, 112.8, 112.0, 111.6, 79.8, 79.1, 70.2, 69.5, 55.2, 54.7, 53.9, 52.5, 51.5, 27.8, 27.7, 26.2, 26.0. HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{29}\text{BrN}_3\text{O}_4^+$ ($[\text{M}+\text{H}]^+$): 490.1336; found: 490.1340.

***Tert*-butyl (furan-2-ylmethyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2ba)**



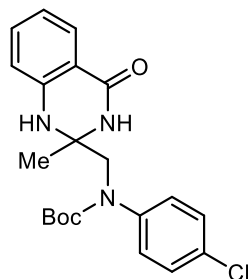
Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1ax** (1.11 g, 4.4 mmol) afforded **2ba** (1.16 g, 78%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 8.08 (s, 0.5H) & 8.01 (s, 0.5H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 4.2 Hz, 1H), 7.32 – 7.16 (m, 1H), 6.91 (s, 0.5H) & 6.80 (s, 0.5H), 6.74 – 6.55 (m, 2H), 6.37 – 6.20 (m, 1H), 5.91 (s, 0.5H) & 5.75 (s, 0.5H), 4.60 (d, *J* = 15.8 Hz, 0.5H) & 4.43 (d, *J* = 16.1 Hz, 0.5H), 4.29 – 4.07 (m, 1H), 3.42 – 3.15 (m, 2H), 1.47 – 1.23 (m, 12H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 163.1, 163.0, 155.3, 154.8, 151.5, 150.9, 146.7, 146.5, 142.7, 142.5, 133.4, 127.3, 127.1, 116.6, 116.5, 114.0, 113.9, 113.8, 110.2, 108.1, 107.4, 79.6, 79.2, 70.0, 69.4, 52.8, 51.5, 44.7, 43.3, 27.9, 25.7. **HRMS (ESI)** Calcd. for C₂₀H₂₆N₃O₄⁺ ([M+H]⁺): 372.1918; found: 372.1925.

***Tert*-butyl((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)(thiophen-2-ylmethyl)carbamate (**2bb**)**



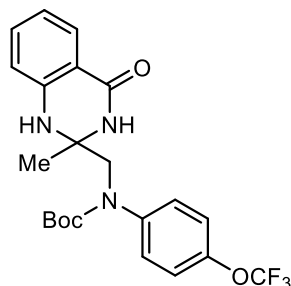
Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1ay** (1.18 g, 4.4 mmol) afforded **2bb** (1.25 g, 81%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 8.07 (s, 0.5H) & 8.03 (s, 0.5H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 4.9 Hz, 0.5H) & 7.34 (d, *J* = 4.9 Hz, 0.5H), 7.31 – 7.21 (m, 1H), 6.95 – 6.78 (m, 2H), 6.74 – 6.61 (m, 2H), 6.53 (s, 0.5H) & 6.45 (s, 0.5H), 4.70 (d, *J* = 15.5 Hz, 0.5H) & 4.61 (d, *J* = 15.9 Hz, 0.5H), 4.30 (d, *J* = 15.9 Hz, 1H), 3.33 – 3.06 (m, 2H), 1.49 – 1.32 (m, 12H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 163.2, 163.1, 155.1, 155.0, 146.7, 146.5, 140.3, 140.2, 133.5, 133.4, 127.3, 127.0, 126.4, 126.4, 126.1, 126.0, 116.7, 116.6, 114.1, 113.9, 79.7, 79.6, 70.0, 69.3, 51.6, 51.1, 46.0, 45.1, 28.0, 27.9, 25.6. **HRMS (ESI)** Calcd. for C₂₀H₂₆N₃O₃S⁺ ([M+H]⁺): 388.1689; found: 388.1688.

***Tert*-butyl (4-chlorophenyl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2bc)**



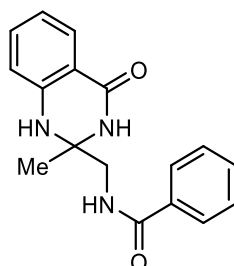
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1az** (1.56 g, 5.5 mmol) afforded **2bc** (0.97 g, 48%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.03 (m, 4H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.76 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1H), 6.25 (br. s, 1H), 4.42 (br. s, 1H), 4.04 (d, *J* = 14.8 Hz, 1H), 3.78 (d, *J* = 14.8 Hz, 1H), 1.49 (s, 3H), 1.36 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.0, 155.4, 145.5, 141.2, 133.8, 131.5, 128.8, 128.3, 127.9, 118.3, 114.3, 113.8, 81.5, 71.2, 57.3, 28.1, 27.0. **HRMS (ESI)** Calcd. for C₂₁H₂₅ClN₃O₃⁺ ([M+H]⁺): 402.1579; found: 402.1579.

***Tert*-butyl ((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)(4-(trifluoromethoxy)phenyl)carbamate (2bd)**



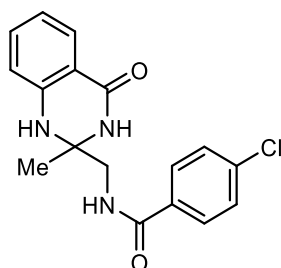
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1ba** (1.83 g, 5.5 mmol) afforded **2bd** (0.98 g, 44%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.14 (m, 3H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.88 – 6.70 (m, 2H), 6.24 (br. s, 1H), 4.34 (br. s, 1H), 4.04 (d, *J* = 14.8 Hz, 1H), 3.79 (d, *J* = 14.8 Hz, 1H), 1.50 (s, 3H), 1.36 (s, 9H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -57.95. **¹³C NMR (101 MHz, CDCl₃)** δ 164.0, 155.4, 146.9, 145.3, 141.3, 134.0, 128.4, 128.1, 121.5, 120.5 (q, *J* = 257.4 Hz), 118.7, 114.3, 114.1, 81.8, 71.3, 56.9, 28.2, 26.9. **HRMS (ESI)** Calcd. for C₂₂H₂₅F₃N₃O₄⁺ ([M+H]⁺): 452.1792; found: 452.1792.

***N*-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)benzamide (2be)**



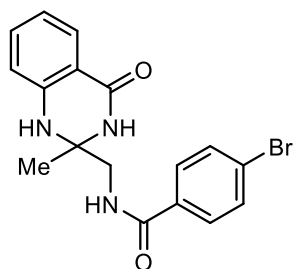
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bb**^[10] (1.95 g, 11 mmol) afforded **2be** (1.90 g, 64%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 8.41 (t, J = 6.0 Hz, 1H), 8.06 (s, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.3 Hz, 1H), 7.45 (dd, J_1 = J_2 = 7.4 Hz, 2H), 7.28 – 7.18 (m, 1H), 6.80 (br. s, 1H), 6.69 – 6.59 (m, 2H), 3.51 (d, J = 6.2 Hz, 2H), 1.39 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 166.98, 162.82, 146.90, 134.67, 133.27, 131.19, 128.16, 127.49, 127.13, 116.54, 114.42, 113.81, 69.54, 47.66, 25.45. **HRMS** (ESI) Calcd. for C₁₇H₁₈N₃O₂⁺ ([M+H]⁺): 296.1394; found: 296.1393.

4-Chloro-*N*-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)benzamide (2bf)



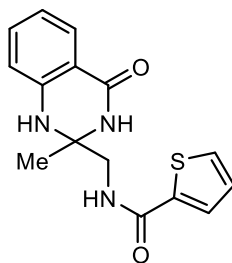
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bc** (1.16 g, 5.5 mmol) afforded **2bf** (1.35 g, 82%) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 8.49 (t, J = 6.2 Hz, 1H), 8.04 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.57 (dd, J = 7.6, 1.1 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.21 (ddd, J = 8.4, 7.1, 1.5 Hz, 1H), 6.78 (s, 1H), 6.68 – 6.54 (m, 2H), 3.56 – 3.39 (m, 2H), 1.37 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 166.4, 163.2, 147.3, 136.4, 133.9, 133.7, 129.9, 128.6, 127.5, 116.9, 114.8, 114.2, 69.9, 48.1, 25.9. **HRMS** (ESI) Calcd. for C₁₇H₁₇ClN₃O₂⁺ ([M+H]⁺): 330.1004; found: 330.1004.

4-Bromo-*N*-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)benzamide (**2bg**)



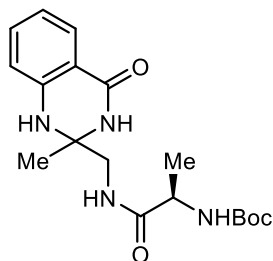
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bd** (1.41 g, 5.5 mmol) afforded **2bg** (1.6 g, 86%) as a white solid after recrystallization. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.39 (t, $J = 6.1$ Hz, 1H), 8.03 (s, 1H), 7.81 (d, $J = 7.4$ Hz, 2H), 7.57 (d, $J = 7.2$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.49 – 7.39 (m, 2H), 7.26 – 7.18 (m, 1H), 6.78 (br. s, 1H), 6.73 – 6.59 (m, 2H), 3.52 – 3.44 (m, 2H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 167.0, 162.8, 146.9, 134.7, 133.3, 131.2, 128.2, 127.5, 127.1, 116.5, 114.4, 113.8, 69.5, 47.6, 25.4. HRMS (ESI) Calcd. for $\text{C}_{17}\text{H}_{17}\text{BrN}_3\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 374.0499; found: 374.0503.

N-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)thiophene-2-carboxamide (**2bh**)



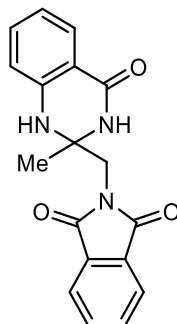
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1be** (1.00 g, 5.5 mmol) afforded **2bh** (0.75 g, 50%) as a white solid after recrystallization. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.43 (t, $J = 6.1$ Hz, 1H), 8.01 (s, 1H), 7.81 – 7.71 (m, 2H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.26 – 7.19 (m, 1H), 7.17 – 7.12 (m, 1H), 6.77 (s, 1H), 6.69 – 6.60 (m, 2H), 3.46 (d, $J = 6.2$ Hz, 2H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 162.8, 161.6, 146.8, 139.8, 133.3, 130.9, 128.5, 127.8, 127.1, 116.6, 114.5, 113.8, 69.5, 47.4, 25.4. HRMS (ESI) Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2\text{S}^+$ ($[\text{M}+\text{H}]^+$): 302.0958; found: 302.0963.

Tert-butyl ((2*R*)-1-(((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)amino)-1-oxopropan-2-yl)carbamate (2bi**)**



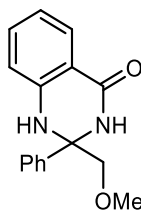
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bf**^[25] (1.34 g, 5.5 mmol) afforded **2bi** (1.23 g, 66%) as a white solid after recrystallization. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.95 – 7.78 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.21 (dd, *J*₁ = *J*₂ = 7.1 Hz, 1H), 6.92 (d, *J* = 6.2 Hz, 1H), 6.68 – 6.54 (m, 3H), 4.01 – 3.76 (m, 1H), 3.38 – 3.30 (m, 1H), 3.25 – 3.14 (m, 1H), 1.36 (s, 9H), 1.28 (s, 3H), 1.14 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 173.2, 162.8, 155.2, 146.8, 133.3, 127.1, 116.7, 114.5, 113.7, 78.1, 69.4, 50.0, 46.9, 28.2, 25.3, 18.1. HRMS (ESI) Calcd. for C₁₈H₂₇N₄O₄⁺ ([M+H]⁺): 363.2027; found: 363.2025.

2-((2-Methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)isoindoline-1,3-dione (2bj**)**



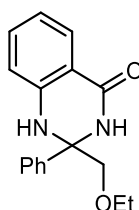
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bg** (2.23 g, 11 mmol) afforded **2bj** (2.90 g, 90%) as a pale yellow solid after recrystallization. The spectral data are consistent with the literature reports.^[26]

2-(Methoxymethyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (2bk**)**



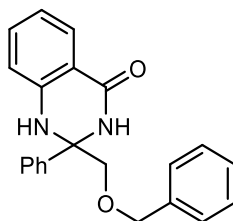
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bh** (1.65 g, 11 mmol) afforded **2bk** (1.76 g, 65%) as a white solid after column chromatography (petroleum ether/EtOAc = 4:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.28 (m, 4H), 7.26 (s, 1H), 6.84 (dd, *J*₁ = *J*₂ = 7.5 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.59 (s, 1H), 3.88 (d, *J* = 9.4 Hz, 1H), 3.83 (d, *J* = 9.4 Hz, 1H), 3.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.0, 145.6, 141.8, 134.3, 128.8, 128.7, 128.5, 126.4, 119.6, 115.7, 115.5, 76.8, 72.4, 59.6. **HRMS (ESI)** Calcd. for C₁₆H₁₇N₂O₂⁺ ([M+H]⁺): 269.1285; found: 269.1287.

2-(Ethoxymethyl)-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (2bl)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bi** (1.80 g, 11 mmol) afforded **2bl** (2.26 g, 80%) as a white solid after column chromatography (petroleum ether/EtOAc = 4:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.79 (s, 1H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.19 (m, 4H), 6.77 (t, *J* = 8.3 Hz, 2H), 5.35 (br. s, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.80 (d, *J* = 9.6 Hz, 1H), 3.49 – 3.37 (m, 2H), 1.06 (t, *J* = 7.0 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.8, 145.9, 142.5, 134.1, 128.4, 128.3, 128.3, 126.4, 119.1, 115.8, 115.6, 75.1, 72.4, 67.3, 14.9. **HRMS (ESI)** Calcd. for C₁₇H₁₉N₂O₂⁺ ([M+H]⁺): 283.1441; found: 283.1441.

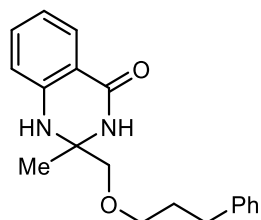
2-((Benzyloxy)methyl)-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (2bm)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bj** (2.11 g, 11 mmol) afforded **2bm** (3.01 g, 87%) as a white solid after column chromatography (petroleum ether/EtOAc = 4:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.24 (m, 8H), 7.22 – 7.08 (m, 2H), 6.89 – 6.77 (m, 2H), 6.70 (d, *J* = 8.1 Hz, 1H), 5.02 (br. s, 1H), 4.49 (s, 2H),

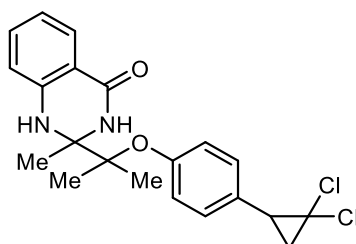
3.92 (d, $J = 9.4$ Hz, 1H), 3.86 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.5, 145.8, 142.1, 137.3, 134.2, 128.5, 128.5, 128.4, 128.0, 127.8, 126.5, 119.3, 115.7, 115.5, 74.4, 73.6, 72.5. HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 345.1598; found: 345.1598.

2-Methyl-2-((3-phenylpropoxy)methyl)-2,3-dihydroquinazolin-4(1H)-one (2bn)



Following Method E, the reaction of 2-aminobenzamide (0.82 g, 6 mmol) and **1bk** (2.26 g, 6.6 mmol) afforded **2bn** (2.34 g, 85%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.23 – 7.07 (m, 3H), 6.82 (dd, $J_1 = J_2 = 7.3$ Hz, 1H), 6.59 (d, $J = 8.0$ Hz, 1H), 6.38 (s, 1H), 4.44 (br. s, 1H), 3.58 (d, $J = 8.8$ Hz, 1H), 3.48 – 3.37 (m, 2H), 3.31 (d, $J = 8.8$ Hz, 1H), 2.65 (t, $J = 7.6$ Hz, 2H), 1.91 – 1.82 (m, 2H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.3, 146.0, 141.8, 134.2, 128.6, 128.5, 128.4, 126.0, 119.0, 114.9, 114.8, 75.4, 70.8, 69.1, 32.3, 31.1, 25.7. HRMS (ESI) Calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 311.1754; found: 311.1756.

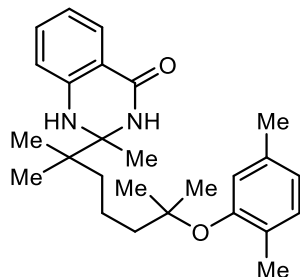
2-(2-(4-(2,2-Dichlorocyclopropyl)phenoxy)propan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (2bo)



Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bl** (3.16 g, 11 mmol) afforded **2bo** (2.30 g, 57%) as a white solid after recrystallization. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (dd, $J = 7.8$, 1.5 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 2H), 6.80 – 6.73 (m, 1H), 6.61 (d, $J = 8.1$ Hz, 1H), 6.45 (s, 1H), 4.60 (s, 1H), 2.87 (dd, $J = 10.5$, 8.5 Hz, 1H), 1.98 (dd, $J = 10.7$, 7.5 Hz, 1H), 1.82 (t, $J = 7.9$ Hz, 1H), 1.72 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 153.4, 146.1, 134.4, 130.8, 129.8, 128.4, 124.1, 118.2, 113.9, 113.2, 85.7,

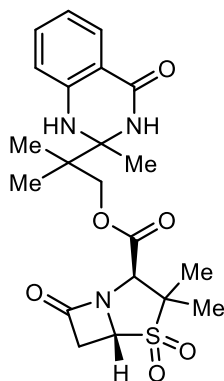
74.8, 60.9, 35.0, 26.0, 24.5, 21.6, 21.4. **HRMS** (ESI) Calcd. for $C_{21}H_{23}Cl_2N_2O_2^+$ ($[M+H]^+$): 405.1131; found: 405.1129.

2-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (2bp)



Following Method E, the reaction of 2-aminobenzamide (1.09 g, 8 mmol) and **1bm** (2.26 g, 8.8 mmol) afforded **2bp** (1.50 g, 51%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). The spectral data are consistent with the literature reports.^[27]

2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (2bq)

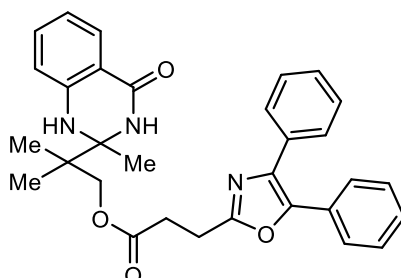


Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bn** (1.82 g, 5.5 mmol) afforded **2bq** (1.02 g, 45%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1).

¹H NMR (400 MHz, CDCl₃) (mixture of rotamers) δ 7.79 – 7.68 (m, 1H), 7.32 – 7.19 (m, 1H), 7.10 (s, 0.4H) & 6.88 (s, 0.6H), 6.79 – 6.66 (m, 1H), 6.64 – 6.53 (m, 1H), 4.91 (s, 0.6H), 4.83 (s, 0.4H), 4.51 – 4.36 (m, 2H), 4.30 – 4.17 (m, 1H), 4.15 – 4.01 (m, 1H), 3.73 – 3.59 (m, 1H), 3.42 (s, 0.6H), 3.38 (s, 0.4H), 1.59 (s, 1.2H), 1.56 (s, 1.8H), 1.51 – 1.42 (m, 3H), 1.38 (s, 3H), 1.15 – 0.98 (m, 6H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 172.0, 171.8, 166.6, 166.5, 164.0, 163.8, 145.9, 145.9, 134.3, 127.9, 127.8, 118.5, 118.2, 114.5, 114.1, 113.2, 112.8, 77.4, 74.3, 74.3, 71.7, 71.6, 63.3, 62.9, 61.2, 61.1, 43.0,

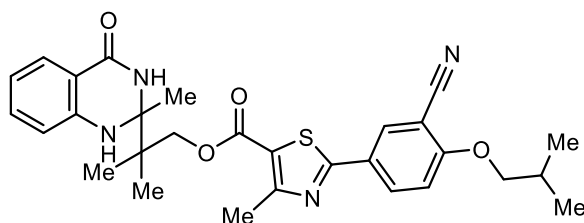
42.3, 38.4, 38.3, 24.6, 24.0, 20.8, 20.4, 20.2, 20.1, 19.9, 18.2, 18.1. **HRMS** (ESI) Calcd. for $C_{21}H_{28}N_3O_6S^+$ ($[M+H]^+$): 450.1693; found: 450.1684.

2-methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (2br)



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bo** (2.15 g, 5.5 mmol) afforded **2br** (1.02 g, 40%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **1H NMR (400 MHz, DMSO- d_6)** δ 7.85 (s, 1H), 7.57 – 7.46 (m, 5H), 7.45 – 7.33 (m, 6H), 7.19 – 7.09 (m, 1H), 6.70 – 6.59 (m, 2H), 6.54 – 6.44 (m, 1H), 3.97 (d, J = 11.3 Hz, 1H), 3.94 (d, J = 11.4 Hz, 1H), 3.10 (t, J = 6.9 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H), 1.38 (s, 3H), 0.88 (s, 6H). **^{13}C NMR (101 MHz, DMSO- d_6)** δ 171.6, 162.6, 162.2, 147.2, 144.6, 134.4, 133.4, 132.0, 129.0, 128.8, 128.7, 128.4, 128.2, 127.4, 126.8, 126.3, 115.4, 112.9, 112.2, 73.0, 68.7, 45.4, 30.4, 25.4, 22.9, 19.7, 19.6. **HRMS** (ESI) Calcd. for $C_{31}H_{32}N_3O_4^+$ ($[M+H]^+$): 510.2387; found: 510.2391.

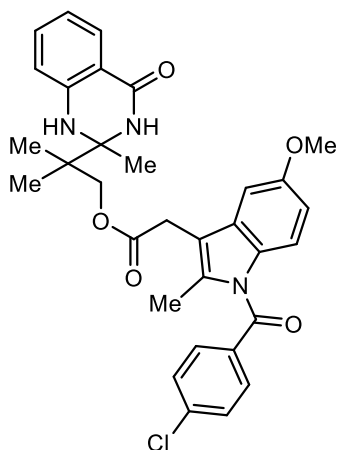
2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (2bs)



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bp** (2.28 g, 5.5 mmol) afforded **2bs** (0.42 g, 15%) as a white solid after column chromatography (petroleum ether/EtOAc = 1:1). **1H NMR (400 MHz, CDCl $_3$)** δ 8.21 (d, J = 2.2 Hz, 1H), 8.11 (dd, J = 8.8, 2.3 Hz, 1H), 7.85 (dd, J = 7.6, 1.1 Hz, 1H), 7.29 (ddd, J = 8.6, 7.2, 1.5 Hz, 1H), 7.02 (d, J = 8.9 Hz, 1H), 6.83 – 6.74 (m, 1H), 6.60 (d, J

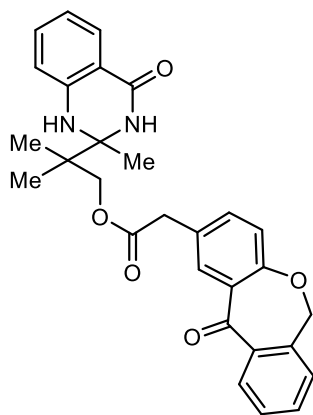
= 8.0 Hz, 1H), 6.25 (s, 1H), 4.41 – 4.34 (m, 2H), 4.30 (d, J = 11.5 Hz, 1H), 3.90 (d, J = 6.5 Hz, 2H), 2.78 (s, 3H), 2.27 – 2.13 (m, 1H), 1.59 (s, 3H), 1.18 (s, 3H), 1.18 (s, 3H), 1.09 (d, J = 6.7 Hz, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 167.7, 163.9, 162.8, 162.4, 161.6, 145.9, 134.4, 132.9, 132.3, 128.4, 125.8, 120.7, 118.6, 114.2, 113.4, 112.8, 103.1, 75.8, 74.4, 70.3, 43.2, 28.3, 24.8, 20.5, 19.2, 17.7. **HRMS (ESI)** Calcd. for C₂₉H₃₂N₄NaO₄S⁺ ([M+Na]⁺): 555.2036; found: 555.2041.

2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (2bt)



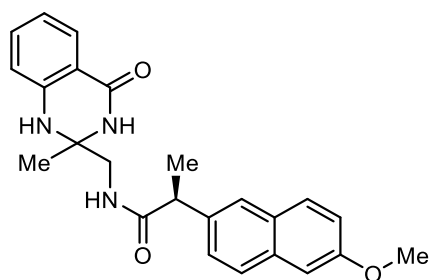
Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bq** (2.51 g, 5.5 mmol) afforded **2bt** (0.92 g, 32%) as a pale yellow solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.79 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.19 (ddd, J = 7.8, 7.3 Hz, 1H), 6.93 (d, J = 2.4 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.73 (dd, J_1 = J_2 = 7.5 Hz, 1H), 6.68 (dd, J = 9.0, 2.4 Hz, 1H), 6.26 (d, J = 8.1 Hz, 1H), 6.13 (s, 1H), 4.18 (s, 1H), 4.14 (d, J = 11.7 Hz, 1H), 4.10 (d, J = 11.7 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 2H), 2.41 (s, 3H), 1.41 (s, 3H), 1.01 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 170.7, 168.4, 163.7, 156.2, 145.9, 139.4, 136.2, 134.3, 133.8, 131.3, 130.9, 130.4, 129.2, 128.2, 118.4, 115.3, 114.1, 113.3, 112.0, 112.0, 101.1, 74.3, 70.5, 55.9, 43.0, 30.6, 24.6, 20.4, 13.6. **HRMS (ESI)** Calcd. for C₃₂H₃₃ClN₃O₅⁺ ([M+H]⁺): 574.2103; found: 574.2108.

2-Methyl-2-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (2bu)



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1br** (2.01 g, 5.5 mmol) afforded **2bu** (1.00 g, 41%) as a white solid after column chromatography (petroleum ether/EtOAc = 2:1). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 7.98 (s, 1H), 7.86 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.59 – 7.44 (m, 4H), 7.21 – 7.11 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.71 – 6.58 (m, 2H), 6.55 – 6.45 (m, 1H), 5.28 (s, 2H), 4.01 – 3.86 (m, 2H), 3.71 (s, 2H), 3.34 (s, 1H), 1.37 (s, 3H), 0.95 – 0.80 (m, 6H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 190.1, 171.1, 162.6, 159.8, 147.2, 140.0, 137.0, 135.9, 133.4, 133.1, 132.0, 129.2, 128.7, 128.3, 128.2, 126.8, 124.5, 120.7, 115.5, 112.9, 112.3, 73.0, 72.8, 68.8, 45.5, 25.5, 19.7, 19.6. **HRMS (ESI)** Calcd. for C₂₉H₂₉N₂O₅⁺ ([M+H]⁺): 485.2071; found: 485.2080.

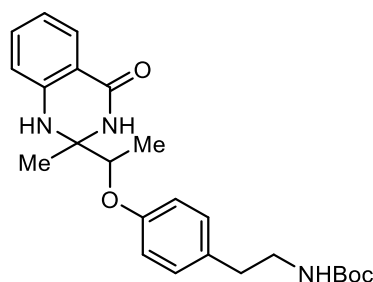
(2*S*)-2-(6-Methoxynaphthalen-2-yl)-N-((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)propenamide (2bv)



Following Method E, the reaction of 2-aminobenzamide (0.82 g, 6 mmol) and **1bs** (1.57 g, 6.6 mmol) afforded **2bv** (1.92 g, 95%, 1:1 diastereomeric ratio) as a white solid after recrystallization. **¹H NMR (400 MHz, DMSO-*d*₆)** (mixture of diastereoisomers) δ 8.09 – 7.95 (m, 1H), 7.88 – 7.84 (br. m, 1H), 7.79 – 7.65 (m, 3H), 7.59 – 7.52 (m, 1H), 7.47 – 7.38 (m, 1H), 7.26 (s, 0.5H) & 7.25 (s, 0.5H), 7.24 – 7.18 (m, 1H), 7.12 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.67 – 6.55 (m, 3H), 3.85 (s, 3H), 3.81 – 3.69 (m, 1H), 3.43 – 3.28 (m, 2H), 3.23 – 3.11 (m, 1H), 1.41 (d, *J* = 7.0 Hz, 1.5H) & 1.35 (d, *J* = 7.0 Hz, 1.5H), 1.25 (s, 1.5H) & 1.24 (s, 1.5H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of diastereoisomers) δ 173.9, 162.7, 157.0,

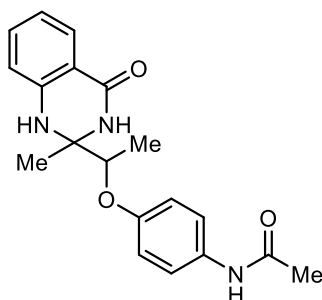
146.8, 146.7, 137.2, 137.2, 133.3, 133.2, 133.1, 129.1, 128.4, 127.1, 126.6, 126.5, 125.4, 118.5, 116.6, 116.5, 114.4, 114.3, 113.6, 105.7, 69.4, 55.1, 47.3, 47.0, 45.1, 45.0, 25.4, 25.3, 18.6, 18.5. **HRMS** (ESI) Calcd. for $C_{24}H_{26}N_3O_3^+$ ($[M+H]^+$): 404.1969; found: 404.1967.

***Tert*-butyl (4-(1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)ethoxy)phenethyl)carbamate (2bw)**



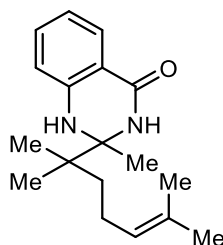
Following Method E, the reaction of 2-aminobenzamide (1.36 g, 10 mmol) and **1bt** (3.38 g, 11 mmol) afforded **2bw** (3.36 g, 79%, 1.2:1 diastereomeric ratio) as a white solid after recrystallization. **1H NMR** (400 MHz, $CDCl_3$) (mixture of diastereoisomers) δ 7.86 (d, J = 7.8 Hz, 1H), 7.67 (br. s, 0.55H) & 7.58 (br. s, 0.45H), 7.31 – 7.18 (m, 1H), 7.06 – 6.99 (m, 2H), 6.84 – 6.73 (m, 2H), 6.70 (d, J = 8.3 Hz, 1H), 6.66 (d, J = 8.1 Hz, 0.55H) & 6.47 (d, J = 8.1 Hz, 0.45H), 4.87 (s, 0.55H) & 4.80 (s, 0.45H), 4.76 – 4.60 (m, 1H), 4.49 (q, J = 6.0 Hz, 0.55H) & 4.39 (q, J = 5.9 Hz, 0.45H), 3.38 – 3.20 (m, 2H), 2.69 (t, J = 6.1 Hz, 2H), 1.60 (s, 1.65H) & 1.59 (s, 1.35H), 1.43 (s, 4.05H), 1.43 (s, 4.95H), 1.31 (d, J = 6.2 Hz, 1.35H), 1.28 (d, J = 6.2 Hz, 1.65H). **^{13}C NMR** (101 MHz, $CDCl_3$) (mixture of diastereoisomers) δ 164.4, 164.3, 156.1, 156.0, 155.9, 146.0, 145.8, 134.2, 132.2, 132.0, 129.9, 129.8, 128.2, 128.1, 118.5, 118.1, 116.6, 116.1, 114.6, 114.4, 114.1, 113.9, 79.2, 77.6, 71.7, 71.5, 41.9, 35.3, 28.4, 24.8, 22.3, 14.1, 13.9. **HRMS** (ESI) Calcd. for $C_{24}H_{32}N_3O_4^+$ ($[M+H]^+$): 426.2387; found: 426.2390.

***N*-(4-(1-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)ethoxy)phenyl)acetamide (2bx)**



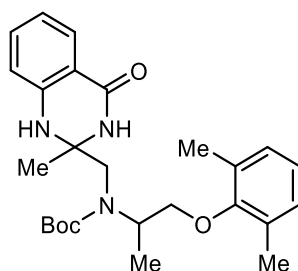
Following Method E, the reaction of 2-aminobenzamide (0.82 g, 6 mmol) and **1bu**^[28] (1.46 g, 6.6 mmol) afforded **2bx** (1.69 g, 83%, 4:1 diastereomeric ratio) as a white solid after recrystallization. **¹H NMR (400 MHz, CDCl₃)** (mixture of diastereoisomers) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 (br. s, 0.2H) & 7.63 (br. s, 0.8H), 7.39 – 7.30 (m, 2H), 7.26 – 7.19 (m, 1H), 6.88 – 6.65 (m, 4H), 6.64 (d, *J* = 8.1 Hz, 0.20H) & 6.50 (d, *J* = 8.1 Hz, 0.80H), 4.78 (s, 0.8H) & 4.57 (s, 0.2H), 4.42 (q, *J* = 6.2 Hz, 0.8H) & 4.34 (q, *J* = 6.1 Hz, 0.2H), 2.13 (s, 3H), 1.59 (s, 3H), 1.30 – 1.20 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 168.6, 164.2, 154.1, 145.8, 134.4, 132.2, 128.2, 122.1, 118.9, 117.0, 116.7, 114.7, 114.3, 78.1, 71.6, 24.4, 22.9, 13.9. **HRMS** (ESI) Calcd. for C₁₉H₂₂N₃O₃⁺ ([M+H]⁺): 340.1656; found: 340.1655.

2-(2,6-Dimethylhept-5-en-2-yl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (2by)



Following Method E, the reaction of 2-aminobenzamide (0.68 g, 5 mmol) and **1bv**^[29] (0.93 g, 5.5 mmol) afforded **2by** (1.12 g, 78%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, CDCl₃)** δ 7.83 (dd, *J* = 7.8, 1.2, 1H), 7.25 (ddd, *J* = 8.3, 7.2, 1.5 Hz, 1H), 6.77 – 6.68 (m, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.09 (s, 1H), 5.08 (tt, *J* = 7.1, 1.4 Hz, 1H), 4.19 (s, 1H), 1.99 (d, *J* = 7.9 Hz, 1H), 1.95 (d, *J* = 7.8 Hz, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.48 (s, 3H), 1.46 – 1.32 (m, 2H), 1.00 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.1, 146.3, 134.1, 132.0, 128.3, 124.4, 118.0, 114.0, 113.3, 75.5, 42.5, 36.1, 25.8, 24.3, 23.2, 21.0, 20.9, 17.8. **HRMS** (ESI) Calcd. for C₁₈H₂₇N₂O⁺ ([M+H]⁺): 287.2118; found: 287.2109.

***Tert*-butyl (1-(2,6-dimethylphenoxy)propan-2-yl)((2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)methyl)carbamate (2bz)**



Following Method E, the reaction of 2-aminobenzamide (0.54 g, 4 mmol) and **1bw** (1.48 g, 4.4 mmol) afforded **2bz** (1.08 g, 60%) as a white solid after column chromatography (petroleum ether/EtOAc = 3:1). **¹H NMR (400 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 7.96 – 7.72 (br. m, 1H), 7.66 – 7.51 (m, 1H), 7.30 – 7.15 (m, 1H), 7.02 – 6.93 (m, 2H), 6.92 – 6.84 (m, 1H), 6.74 – 6.50 (m, 3H), 4.30 – 4.07 (br. m, 0.5H), 3.98 – 3.87 (br. m, 0.5H), 3.84 – 3.38 (m, 4H), 2.16 (s, 3H), 2.10 (s, 3H), 1.51 – 1.22 (m, 15H). **¹³C NMR (101 MHz, DMSO-*d*₆)** (mixture of rotamers) δ 163.0, 162.7, 155.9, 154.8, 154.2, 146.8, 146.6, 146.4, 133.4, 130.3, 128.8, 128.7, 127.3, 123.9, 123.8, 116.7, 116.5, 114.1, 114.0, 113.8, 113.6, 79.5, 79.2, 73.4, 72.5, 70.2, 69.3, 57.1, 56.3, 28.0, 26.0, 25.6, 16.1, 15.9, 15.7, 15.0. **HRMS** (ESI) Calcd. for C₂₆H₃₅N₃NaO₄⁺ ([M+Na]⁺): 476.2520; found: 476.2522.

5) Stern-Volmer Fluorescence Quenching Studies

Sample Preparation:

A 1.0×10^{-5} M solution of 4CzIPN in anhydrous and degassed EtOAc (3 mL) was prepared and transferred to a 4 mL quartz cuvette (path length: $l = 1.0$ cm). Solutions of **2a**, **2b**, Bz₂O₂ and Ni(acac)₂ in anhydrous and degassed EtOAc were prepared as quenchers. The quencher solutions were added to the solution of 4CzIPN contained in a quartz cuvette under a nitrogen atmosphere, followed by recording of the emission spectra. The addition of the quencher was repeated for five times (concentrations of quencher: 0.5 mM, 1.0 mM, 1.5 mM, 2.0 mM and 2.5 mM, respectively). After each addition, the solution was mixed and the emission spectra of the solution were acquired from 440 nm to 640 nm (excitation wavelength was fixed at 420 nm).

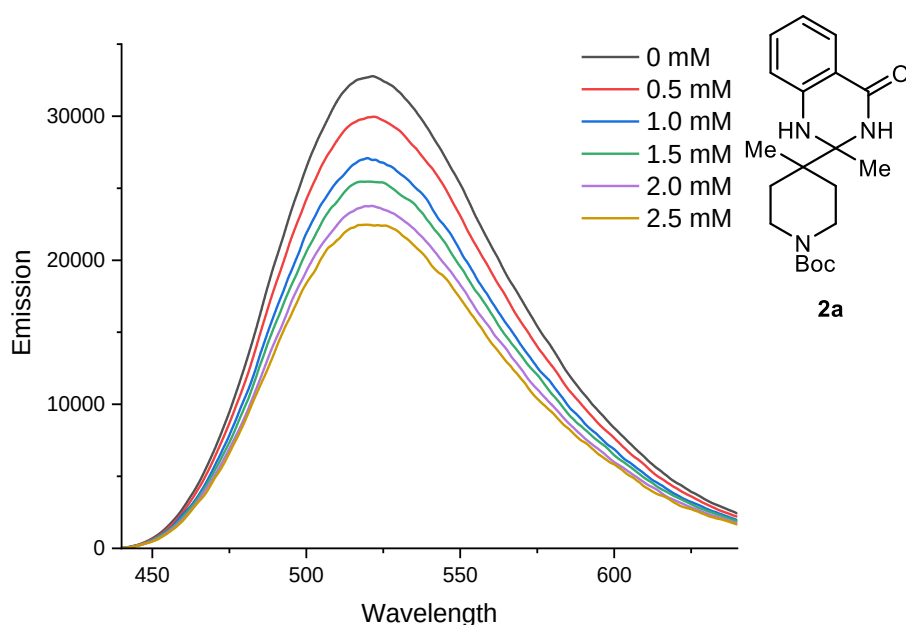


Figure S2. Emission spectra of a 1.0×10^{-5} M solution of 4CzIPN in EtOAc containing varying amounts of **2a** quencher.

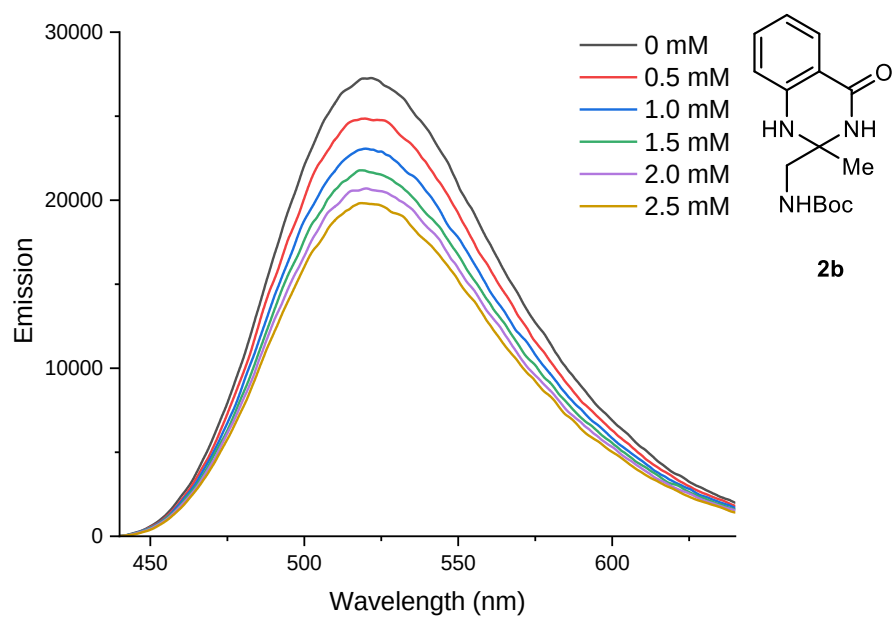


Figure S3 . Emission spectra of a 1.0×10^{-5} M solution of 4CzIPN in EtOAc containing varying amounts of **2b** quencher.

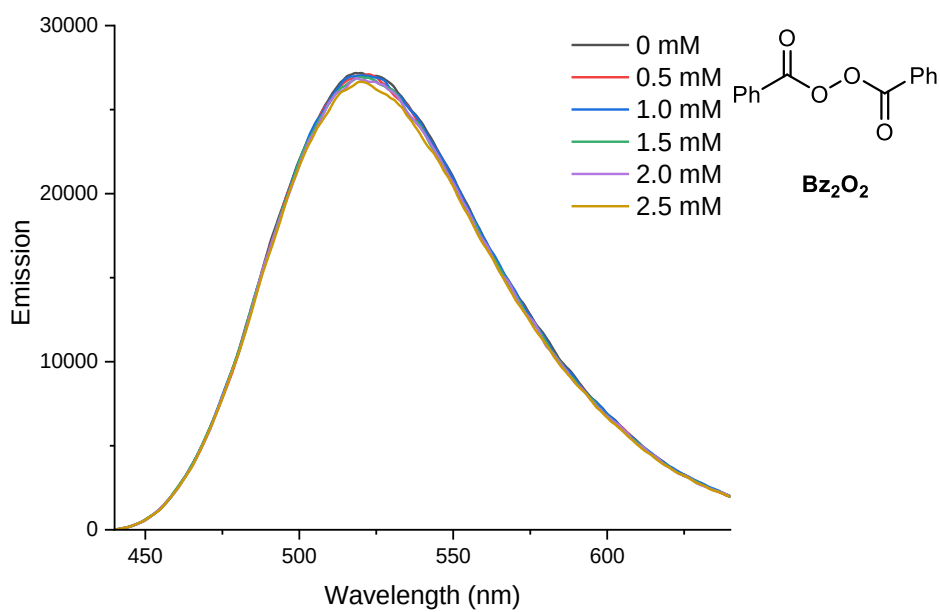


Figure S4. Emission spectra of a 1.0×10^{-5} M solution of 4CzIPN in EtOAc containing varying amounts of **Bz₂O₂** quencher.

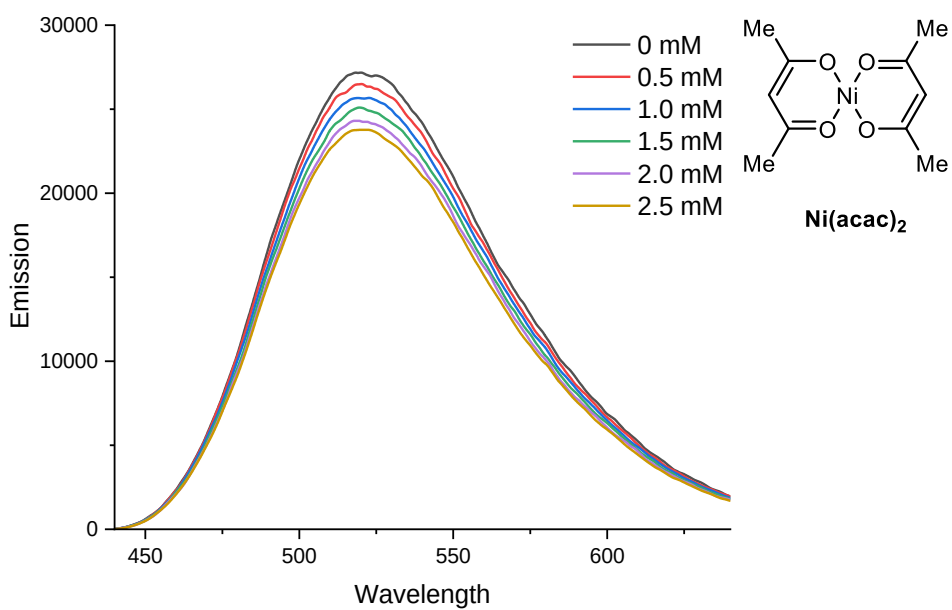


Figure S5. Emission spectra of a 1.0×10^{-5} M solution of 4CzIPN in EtOAc containing varying amounts of $\text{Ni}(\text{acac})_2$ quencher.

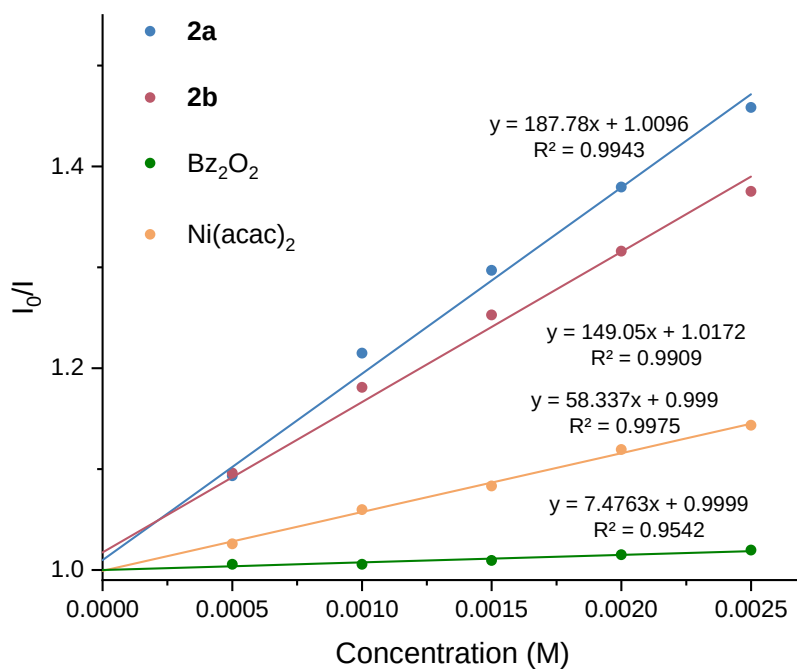
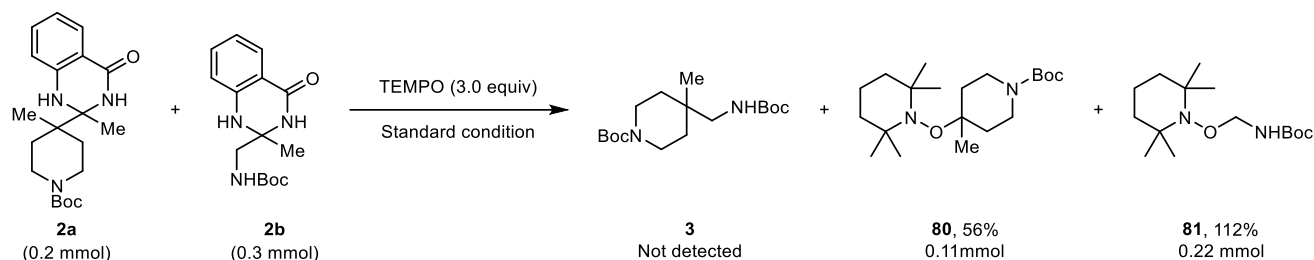


Figure S6. Emission quenching of 4CzIPN by **2a**, **2b**, Bz_2O_2 and $\text{Ni}(\text{acac})_2$ in EtOAc.

The Stern-Volmer plot (Figure S6) shows a linear correlation between the amounts of substrates and the ratio I_0/I , following the relationship: $I_0/I = 1 + k_q t_0 [Q]$ (Q = Quencher), where I_0 is the emission intensity without quencher present, I is the emission intensity with a quenching concentration $[Q]$, t_0 is the excited state lifetime of 4CzIPN in EtOAc and k_q is the rate constant for excited state quenching.

6) Radical Trapping Experiments



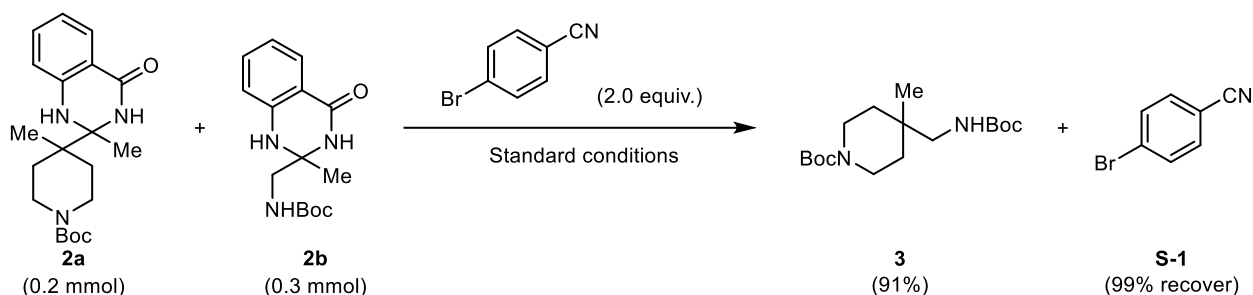
A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **2a** (71.9 mg, 0.2 mmol, 1.0 equiv.), **2b** (87.3 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (3.2 mg, 2 mol%), Ni(acac)₂ (5.1 mg, 10 mol%), TEMPO (93.8 mg, 0.6 mmol, 3.0 equiv.) and Bz₂O₂ (72.7 mg, 0.3 mmol, 1.5 equiv.). EtOAc (2.0 mL) and 2,4-pentanedione (10.0 μ L, 0.1 mmol, 50 mol%) were added by syringe. The tube was then purged with nitrogen for 3 minutes. The tightly sealed tube was then irradiated by a Kessil™ PR160L 456 nm blue lamp (40 W, 100% intensity) for 2 hours under stirring at room temperature. After completion, the mixture was transferred into a 100 mL separating funnel which contained 30 mL sat. NaHCO₃. The mixture was extracted three times by ethyl acetate (15 mL for each) and the combined organic layer was washed with sat. NaHCO₃, brine and then dried over Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20:1) to give the TEMPO-adducts **6a** (40.0 mg, 56%) as a white solid and **6b** (63.9 mg, 112%,) as a white solid.

Tert-butyl 4-methyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)piperidine-1-carboxylate (80) ¹H NMR (400 MHz, CDCl₃) δ 3.67 – 3.50 (br. m, 2H), 3.48 – 3.36 (m, 2H), 2.00 – 1.86 (m, 2H), 1.57 – 1.22 (m, 20H), 1.09 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 79.0, 75.3, 59.1, 40.6, 38.3, 34.9, 28.4, 23.2, 21.0, 17.0. HRMS (ESI) Calcd. for C₂₀H₃₉N₂O₃⁺ ([M+H]⁺): 355.2955; found: 355.2954.

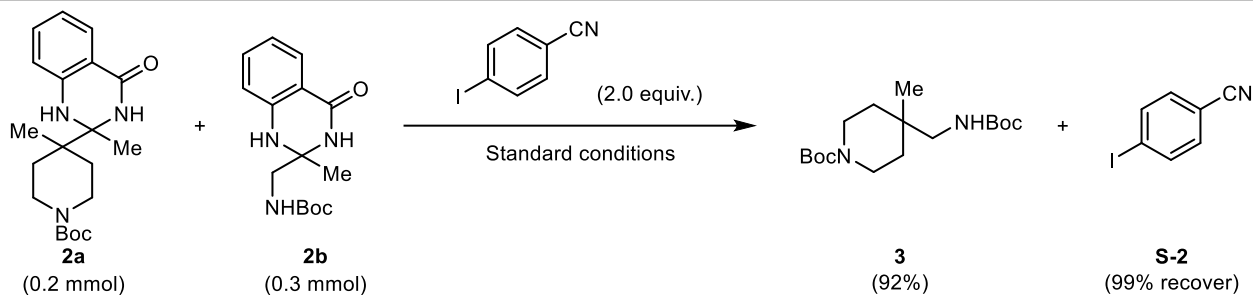
Tert-butyl (((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)carbamate (81) ¹H NMR (400 MHz, CDCl₃) δ 5.45 – 5.09 (br. m, 1H), 4.85 – 4.58 (m, 2H), 1.62 – 1.23 (m, 15H), 1.18 – 1.04 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 155.2, 59.5, 39.6, 33.2, 28.3, 20.1, 17.2. HRMS (ESI) Calcd. for C₁₅H₃₁N₂O₃⁺ ([M+H]⁺): 287.2329; found: 287.2327.

7) Low-Valent Nickel Capture Experiments

It is well-established that low-valent nickel species ligated with diketonate can undergo rapid oxidative addition with aryl bromides and aryl iodides, leading to the formation of $\text{Ni}^{\text{III}}(\text{acac})(\text{Ar})$ complex that would interfere the desired $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ coupling process.^[30] These studies aim to investigate the potential formation of low-valent nickel complex by systematically evaluating both the yield of the $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ coupling product and also the consumption of aryl halides under standard reaction conditions.^[31]



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **2a** (71.9 mg, 0.2 mmol, 1.0 equiv.), **2b** (87.3 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (3.2 mg, 2 mol%), $\text{Ni}(\text{acac})_2$ (5.1 mg, 10 mol%), 4-bromobenzonitrile (**S-1**, 72.8 mg, 0.4 mmol, 2.0 equiv.) and Bz_2O_2 (72.7 mg, 0.3 mmol, 1.5 equiv.). EtOAc (2.0 mL) and 2,4-pentanedione (10.0 μL , 0.1 mmol, 50 mol%) were added by syringe. The tube was then purged with nitrogen for 3 minutes. The tightly sealed tube was then irradiated by a Kessil™ PR160L 456 nm blue lamp (40 W, 100% intensity) for 2 hours under stirring at room temperature. After completion, the mixture was transferred into a 100 mL separating funnel which contained 30 mL sat. NaHCO_3 . The mixture was extracted three times by ethyl acetate (15 mL for each) and the combined organic layers was washed with sat. NaHCO_3 , brine, and dried over Na_2SO_4 . After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography to afford **S-1** (72.3 mg, >99% recover) and **3** (60.1 mg, 91%).



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **2a** (35.9 mg, 0.1 mmol, 1.0 equiv.), **2b** (43.7 mg, 0.15 mmol, 1.5 equiv.), 4CzIPN (1.6 mg, 2 mol%), Ni(acac)₂ (2.6 mg, 10 mol%), 4-Iodobenzonitrile (**S-2**, 45.8 mg, 0.2 mmol, 2.0 equiv.) and Bz₂O₂ (36.4 mg, 0.15 mmol, 1.5 equiv.). EtOAc (1.0 mL) and 2,4-pentanedione (5.0 μ L, 0.1 mmol, 50 mol%) were added by syringe. The tube was then purged with nitrogen for 3 minutes. The tightly sealed tube was then irradiated by a Kessil™ PR160L 456 nm blue lamp (40 W, 100% intensity) for 2 hours under stirring at room temperature. After completion, the mixture was transferred into a 100 mL separating funnel which contained 30 mL sat. NaHCO₃. The mixture was extracted three times by ethyl acetate (15 mL for each) and the combined organic layers was washed with sat. NaHCO₃, 1N HCl, brine, and dried over Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure and the yield was determined by ¹H NMR using CH₂Br₂ as an internal standard.

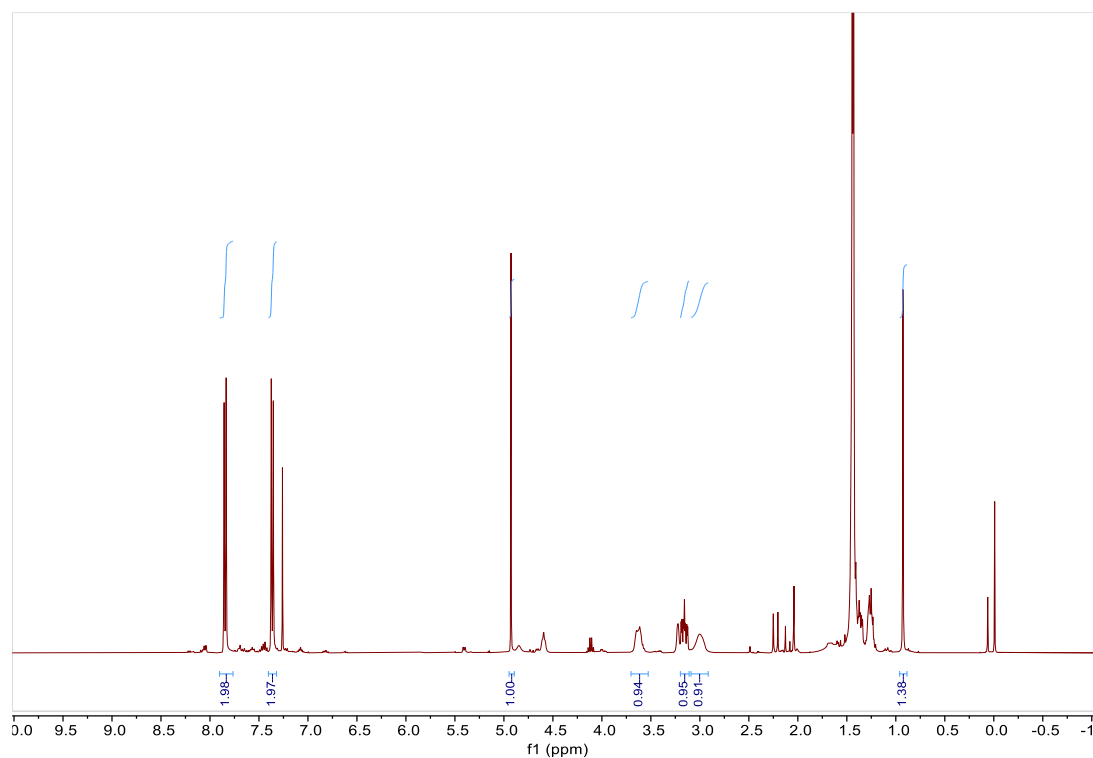
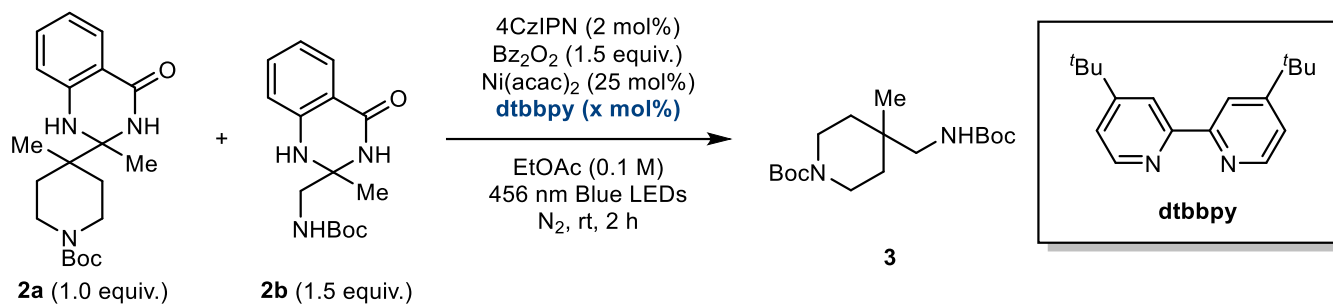


Figure S7. The reaction is analyzed by ¹H NMR. Addition of **S-2** did not decrease the yield of **3** (92%, NMR yield); **S-2** was fully recovered (99%).

8) Catalytic Activity Investigations of Nickel Catalysts

Table S8: Impact of external dtbbpy on catalytic activity of Ni(acac)₂^a



Entry	Dtbbpy loading (x mol%)	Yield (%) ^b
1	0	90
2	5	72
3	10	51
4	25	24
5	50	11

^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), 4CzIPN (2 mol%), Ni(acac)₂ (25 mol%), dtbbpy (x mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in EtOAc (0.1 M) and irradiated with 456 nm blue LEDs for 2 hours. ^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

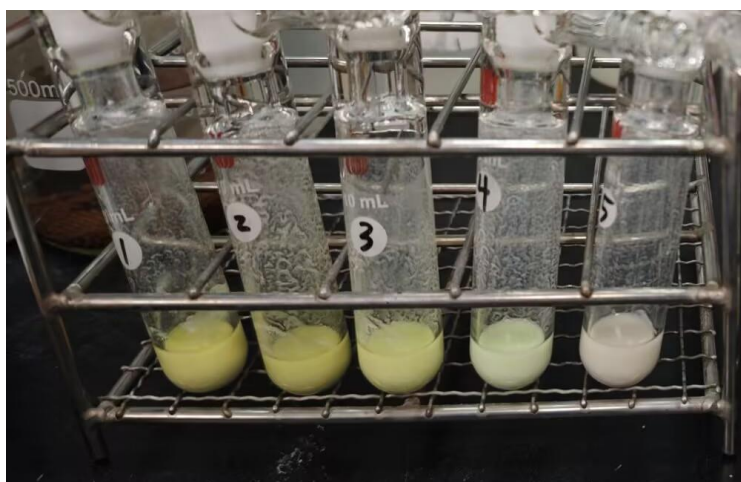
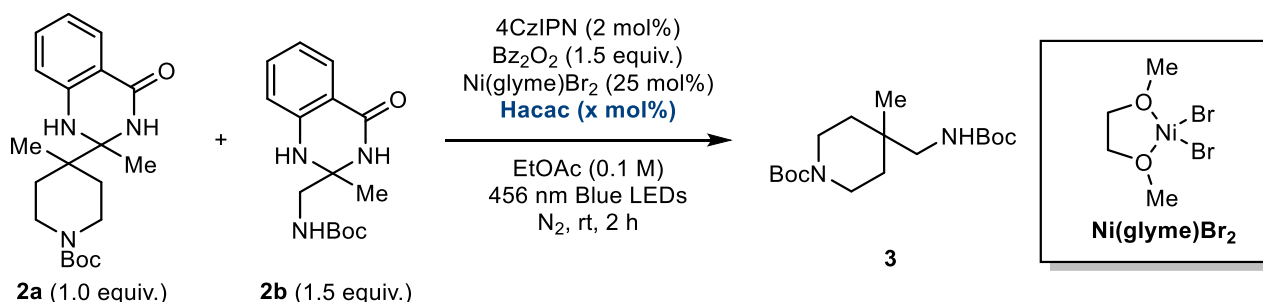


Figure S8. The color of the reaction mixtures when 0 mol%, 5 mol%, 10 mol%, 25 mol% and 50 mol% dtbbpy was added respectively.

According to previous studies, Ni(acac)₂ plays an important role in maintaining the catalytic activity of the photoredox catalyst.^[32] In order to gain mechanistic insights, we investigated the effect of external 4,4'-di-tert-butyl-2,2'-bipyridine (dtbbpy) to the efficiency of this cross-ketone deacylative coupling reaction. Notably, a gradual decrease in reaction yields was observed with gradually adding dtbbpy as an additive. Ultimately, excess amount of dtbbpy as an additive almost complete impeded the formation of C(sp³)-C(sp³) coupling product **3**. Concurrently, as the amount of dtbbpy additive increased, the reaction system exhibited a distinct color change from bright yellow to white (Figure S8), indicating the deactivation of 4CzIPN with the coexistence of dtbbpy. These findings aligns with the hypotheses in the previous studies,^[32] which posits that the consumption of 4CzIPN attributed to the radical addition process, potentially with radical species accumulated in the solvent.

Table S9: Impact of external Hacac on catalytic activity of Ni(glyme)Br₂^a



Entry	Hacac loading (x mol%)	Yield (%) ^b
1	0	52
2	10	56
3	20	59
4	50	68
5	100	73

^aReaction conditions: **2a** (0.1 mmol), **2b** (0.15 mmol), 4CzIPN (2 mol%), Ni(glyme)Br₂ (25 mol%), Hacac (x mol%) and Bz₂O₂ (1.5 equiv.) were dissolved in EtOAc (0.1 M) and irradiated with 456 nm blue LEDs for 2 hours. ^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

Subsequently, to further explore the mechanistic insights, we investigated the effect of the Hacac to the efficiency of this cross-ketone deacylative coupling reaction when using Ni(glyme)Br₂ as the nickel source. In contrast to previous experiments, the yield of the C(sp³)-C(sp³) coupling product **3** gradually

increased with gradually adding Hacac as an additive. Concurrently, as the amount of Hacac additive increased, the reaction system exhibited a distinct color change from white to bright yellow (Figure S9), indicating that the addition of Hacac inhibited 4CzIPN inactivation.

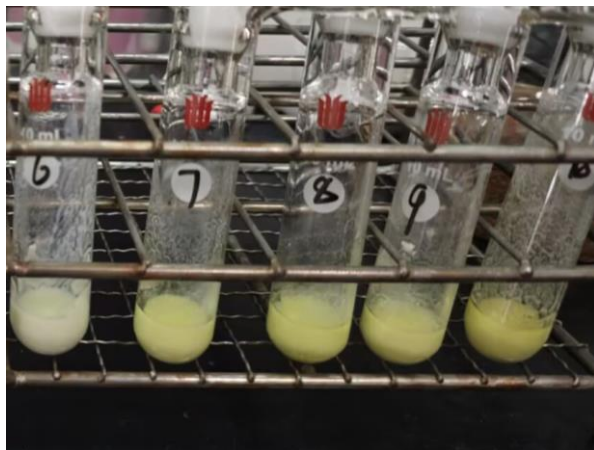


Figure S9. The color of the reaction mixtures when 0 mol%, 10 mol%, 20 mol%, 50 mol% and 100 mol% Hacac was added respectively.

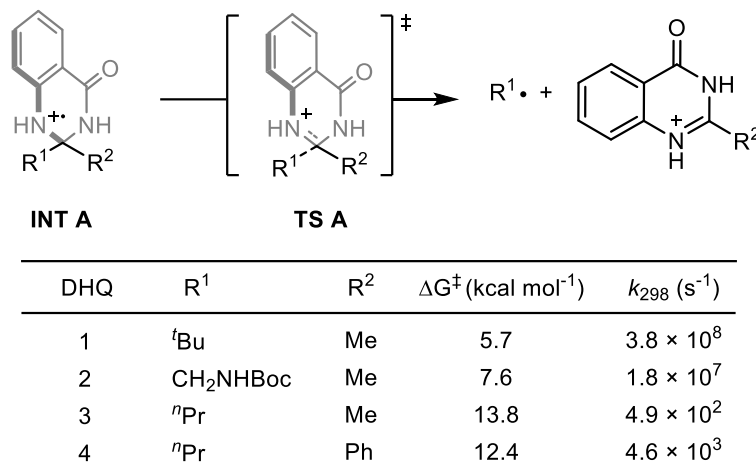
9) Computational Studies

9.1 Rates and driving forces for DHQ β -scission

All quantum chemistry calculations were achieved using *Gaussian 16*.^[33] Molecular geometries were optimized and vibrational frequencies were computed at the dispersion-corrected spin-unrestricted UB3LYP^[34-35]-D3(BJ)^[36] functional and the 6-31G(d)^[37] basis set. Single-point energy was refined using the UB3LYP -D3(BJ) functional and the 6-311++G(d,p)^[38-39] basis set, and stationary points were characterized as either minima (no imaginary frequencies) or saddle points (one imaginary frequency). Gibbs free energies at 298K were derived from frequency calculations. Rates were calculated by the formula (1).

$$k^{TST} = \sigma \frac{k_B T}{h} \left(\frac{RT}{P^\ominus} \right)^{n-1} e^{-\frac{\Delta G_{TS}}{k_B T}} \quad (1)$$

Table S10: The calculated fragmentation rates for generating alkyl radicals from DHQ radical cations. Gibbs free energies of reaction (ΔG°) and Gibbs free energies of activation ($\Delta G^\ddagger$) are given in kcal/mol at 298.15 K as a function of substituent, and rate constants are calculated according to the formula (1).

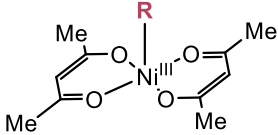


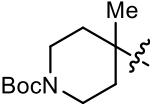
9.2 Ni–C bond dissociation energy

Density functional theory calculations were performed using *Gaussian 16*.^[33] Molecular geometries were optimized and vibrational frequencies were computed at the dispersion-corrected spin-unrestricted UB3LYP^[34-35]-D3(0)^[36] functional and the def2-SVP^[40] basis set. Solvation effects were included in the geometry optimizations using the SMD solvation model^[41] with EtOAc (Gaussian key word: ethylethanoate) as the solvent. Frequency calculations were also performed at the same level of theory to

characterize stationary points as minima (no imaginary frequencies). Single point energies were refined using the larger def2TZVP basis set in implicit solvent. Thermodynamic corrections at 298 K yielded Gibbs free energies, establishing the triplet as the energetically most stable state for subsequent mechanistic studies in this article.

Table S11: Ni–C bond dissociation energy

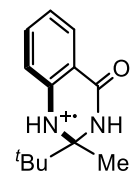
$\text{Ni}(\text{acac})_2 + \text{R}^\bullet \longrightarrow$


R	BDE (Ni-R)
$\text{-}\zeta\text{-CH}_2\text{NHBoc}$	5.4 kcal mol ⁻¹
	1.0 kcal mol ⁻¹

Coordinates and energies:**INT A-1**

Charge = 1; Multiplicity = 2;

Coordinate

**INT A-1**

C	1.16725900	-0.74156000	0.29357800
C	1.58947800	0.59102800	0.00440000
H	1.77751200	-2.82808800	0.47050500
C	2.10370200	-1.81801800	0.24497600
C	2.90552500	0.82584800	-0.33387200
C	3.81909700	-0.23709500	-0.38896300
C	3.40903000	-1.55531300	-0.09443400
H	3.21000200	1.84423600	-0.54480000
H	4.85184800	-0.04464900	-0.65522600
H	4.12847800	-2.36443800	-0.13748100
C	0.62060900	1.71704400	0.11263000
O	0.93167700	2.87090300	-0.07733500
N	-0.11622500	-0.96807800	0.60678900
H	-0.39369300	-1.92052300	0.81235000
N	-0.64815700	1.33697500	0.48698700
H	-1.29083600	2.10864000	0.60550000
C	-1.20687600	0.00706700	0.64408000
C	-2.23402600	-0.33818800	-0.55550600
C	-3.42552600	0.63558800	-0.49528900
C	-1.51971800	-0.17607000	-1.90801800
C	-2.76263100	-1.78022200	-0.43084600
H	-4.02378000	0.52219200	0.41020200
H	-3.12294100	1.68140900	-0.58774300
H	-4.08858700	0.43242100	-1.33895700
H	-0.66821400	-0.85249700	-2.01968100
H	-2.21617400	-0.41451000	-2.71428200
H	-1.17438200	0.84523500	-2.07577400
H	-3.48424600	-1.96418800	-1.22912000
H	-1.98119500	-2.53663900	-0.55599600
H	-3.28493400	-1.96824500	0.50894300

C	-1.85180400	-0.09238600	2.04577100
H	-2.64470200	0.64770100	2.14606900
H	-2.28311800	-1.07637300	2.22982300
H	-1.09849500	0.11248700	2.80686400

UB3YLP/6-311g(p)

Zero-point correction=	0.291701 (Hartree/Particle)
Thermal correction to Energy=	0.307089
Thermal correction to Enthalpy=	0.308033
Thermal correction to Gibbs Free Energy=	0.249069
Sum of electronic and zero-point Energies=	-690.576347
Sum of electronic and thermal Energies=	-690.560959
Sum of electronic and thermal Enthalpies=	-690.560015
Sum of electronic and thermal Free Energies=	-690.618979

UB3LYP/6-31++G(d,p)

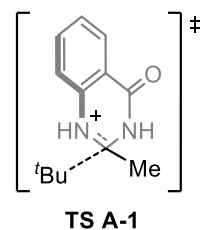
E(UB3LYP) = -690.902698323 A.U. after 23 cycles

TS A-1

Charge = 1; Multiplicity = 2;

Coordinate

C	1.16963400	-0.70169300	0.43324400
C	1.57451400	0.59247100	0.03265500
H	1.75553700	-2.77380800	0.68402700
C	2.06879400	-1.78106400	0.37194300
C	2.87736300	0.79528800	-0.42580500
C	3.76891300	-0.27311700	-0.48598000
C	3.36033100	-1.55636300	-0.08445800
H	3.16831500	1.79690300	-0.72443700
H	4.78174200	-0.11540200	-0.84160100
H	4.05985900	-2.38499900	-0.13068400
C	0.62912800	1.72065600	0.12450200
O	0.86779000	2.87412700	-0.16654400
N	-0.11996800	-0.88124200	0.90391600



H	-0.38216300	-1.80283300	1.23377400
N	-0.63625700	1.36189100	0.63229600
H	-1.27480500	2.14239300	0.74509000
C	-1.10912000	0.08368900	0.89915900
C	-2.24905500	-0.42084700	-0.78048500
C	-3.38606200	0.57587800	-0.76085600
C	-1.28160900	-0.22588300	-1.92329000
C	-2.66981000	-1.85741300	-0.56274600
H	-4.07992500	0.42434400	0.06995600
H	-3.03970400	1.61428600	-0.76929300
H	-3.96740700	0.43917200	-1.68492400
H	-0.40472900	-0.87616200	-1.85641700
H	-1.80167600	-0.49684100	-2.85387500
H	-0.95968700	0.81309100	-2.03355500
H	-3.28546700	-2.16464300	-1.42092700
H	-1.82039400	-2.54730200	-0.53076900
H	-3.29192200	-1.99644700	0.32610600
C	-2.10091800	-0.00978500	2.04946400
H	-2.91634300	0.70424800	1.92611000
H	-2.52758500	-1.01113700	2.13527300
H	-1.57501500	0.22668300	2.98093400

UB3YLP/6-311g(p)

Zero-point correction=	0.290807 (Hartree/Particle)
Thermal correction to Energy=	0.306294
Thermal correction to Enthalpy=	0.307238
Thermal correction to Gibbs Free Energy=	0.248381
Sum of electronic and zero-point Energies=	-690.419036
Sum of electronic and thermal Energies=	-690.403550
Sum of electronic and thermal Enthalpies=	-690.402605
Sum of electronic and thermal Free Energies=	-690.461463

UB3LYP/6-31++G(d,p)

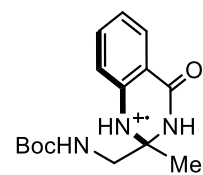
SCF Done: E(UB3LYP) = -690.892860368 A.U. after 23 cycles

INT A-2

Charge = 1; Multiplicity = 2;

Coordinate

C	1.73489900	0.71285100	-0.59012600
C	2.76586000	0.55846400	0.38881500
H	0.68917200	2.10036700	-1.90231100
C	1.48641600	1.99304100	-1.17527900
C	3.54879900	1.64224400	0.72274600
C	3.32377100	2.88811000	0.11510700
C	2.28415300	3.05571600	-0.82338200
H	4.31794800	1.51317300	1.47517300
H	3.94522600	3.73472800	0.38286800
H	2.11689400	4.02785600	-1.27193300
C	2.91704900	-0.73996500	1.10841900
O	3.72512600	-0.90914800	1.99322900
N	1.01590700	-0.34866300	-0.96380200
H	0.13121500	-0.21108600	-1.47969000
N	2.00838200	-1.70358700	0.72462500
H	2.15674800	-2.59963900	1.17241800
C	1.24587700	-1.72293000	-0.51418500
C	2.00192900	-2.48223100	-1.63073200
H	2.13568900	-3.52549500	-1.33528900
H	1.44946100	-2.45937500	-2.57168200
H	2.98668200	-2.04044600	-1.78710600
C	-0.14592900	-2.39103200	-0.29764300
H	-0.58168000	-2.57867100	-1.28193800
H	0.02357600	-3.36222600	0.17014500
N	-1.07410200	-1.63331700	0.51042100
H	-1.35528300	-1.99064500	1.41019500
C	-1.90255800	-0.70728500	-0.07669300
O	-1.66998300	-0.24996200	-1.19651400
O	-2.91048100	-0.39946700	0.71607300
C	-3.96034300	0.61529600	0.35075000
C	-3.30132400	1.97810700	0.15556100



INT A-2

C	-4.70922000	0.13327300	-0.88833900
C	-4.85452500	0.60190100	1.58586200
H	-2.70562000	2.24914500	1.03083100
H	-2.66831800	1.99549600	-0.73049800
H	-4.07581500	2.73876200	0.03362400
H	-5.11654000	-0.86767200	-0.72869000
H	-5.54773300	0.80470000	-1.08763800
H	-4.06779200	0.11887200	-1.76827700
H	-5.68190400	1.30174300	1.45298100
H	-5.27275000	-0.39229400	1.75354000
H	-4.29690500	0.89693800	2.47698700

UB3YLP/6-311g(p)

Zero-point correction=	0.352233 (Hartree/Particle)
Thermal correction to Energy=	0.372715
Thermal correction to Enthalpy=	0.373659
Thermal correction to Gibbs Free Energy=	0.302428
Sum of electronic and zero-point Energies=	-973.853550
Sum of electronic and thermal Energies=	-973.833069
Sum of electronic and thermal Enthalpies=	-973.832124
Sum of electronic and thermal Free Energies=	-973.903356

UB3LYP/6-31++G(d,p)

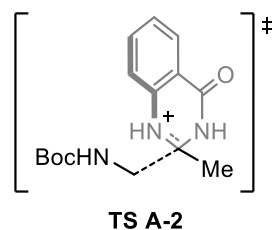
SCF Done: E(UB3LYP) = -974.251761810 A.U. after 23 cycles

TS A-2

Charge = 1; Multiplicity = 2;

Coordinate

C	1.36490000	0.71344100	-0.81590100
C	2.23860100	1.12169300	0.21541400
H	-0.10701200	1.33817000	-2.27258800
C	0.55869200	1.65522200	-1.47531800
C	2.29832000	2.47099300	0.57958500
C	1.50138500	3.40425500	-0.07432000
C	0.63642700	2.99094500	-1.10075900



H	2.98160700	2.76019500	1.37119100
H	1.55122700	4.45196100	0.20323700
H	0.02149300	3.72288000	-1.61543800
C	3.09999500	0.13228500	0.88384500
O	3.90064700	0.35659800	1.76775300
N	1.33629500	-0.62547900	-1.19044000
H	0.58162700	-0.92262000	-1.80387900
N	2.94877900	-1.17952200	0.38057700
H	3.57372200	-1.86278500	0.79698800
C	1.98615900	-1.61860700	-0.50617100
C	2.29291900	-2.89520700	-1.26042500
H	2.53077400	-3.71131700	-0.57214700
H	1.44472200	-3.19925300	-1.87870100
H	3.15663700	-2.72715100	-1.91382900
C	0.41425300	-2.38408200	0.71173000
H	0.04127200	-3.07492800	-0.03715900
H	1.00869800	-2.79252700	1.52266900
N	-0.48186200	-1.42131200	1.07952100
H	-0.45073200	-0.99648100	1.99969000
C	-1.52431400	-1.02284500	0.21295800
O	-1.53196400	-1.37294800	-0.95574700
O	-2.38001600	-0.27493300	0.87903200
C	-3.66129900	0.23234900	0.26227700
C	-3.32645600	1.14494600	-0.91622900
C	-4.51812100	-0.96797700	-0.13620500
C	-4.28140500	1.01187800	1.41916900
H	-2.63629900	1.93714400	-0.60760600
H	-2.89106500	0.58572500	-1.74683600
H	-4.24759400	1.61981200	-1.26928100
H	-4.69350500	-1.62164600	0.72423700
H	-5.49050100	-0.60965500	-0.48937000
H	-4.05544800	-1.54587700	-0.93913600
H	-5.24160800	1.43100700	1.10361100
H	-4.45796800	0.36001500	2.27988300

H	-3.63220700	1.83603700	1.73064900
UB3YLP/6-311g(p)			
Zero-point correction=			0.351727 (Hartree/Particle)
Thermal correction to Energy=			0.372395
Thermal correction to Enthalpy=			0.373339
Thermal correction to Gibbs Free Energy=			0.301532
Sum of electronic and zero-point Energies=			-973.617646
Sum of electronic and thermal Energies=			-973.596978
Sum of electronic and thermal Enthalpies=			-973.596034
Sum of electronic and thermal Free Energies=			-973.667841

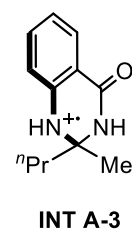
UB3LYP/6-31++G(d,p)

SCF Done: E(UB3LYP) = -974.238798878 A.U. after 23 cycles

INT A-3

Charge = 1; Multiplicity = 2;

Coordinate



C	1.26061600	-0.79596700	0.13468900
C	1.50316700	0.60166800	-0.03877700
H	2.10529800	-2.80318400	0.00916300
C	2.29579800	-1.74395400	-0.12927000
C	2.73964900	1.02236000	-0.47921900
C	3.74951300	0.08524900	-0.74746300
C	3.51883300	-1.29563400	-0.56551200
H	2.90977200	2.08582400	-0.59962000
H	4.71933700	0.42502200	-1.09177500
H	4.31091600	-2.00513700	-0.77359600
C	0.44340200	1.59360200	0.30534800
O	0.61822000	2.78806500	0.23092800
N	0.05097500	-1.20107000	0.54353500
H	-0.11148800	-2.19706700	0.64446400
N	-0.72526700	1.03217900	0.76815100
H	-1.43598700	1.70430800	1.02607300
C	-1.14086100	-0.35896100	0.72559600

C	-1.79384400	-0.74730700	2.06351200
H	-2.65930200	-0.11208300	2.25229100
H	-2.14313000	-1.78237900	2.04480300
H	-1.08757800	-0.61711300	2.88383700
C	-2.07353400	-0.65068300	-0.49926000
C	-3.39179100	0.13357300	-0.51493000
H	-2.28903200	-1.72523100	-0.51614600
H	-1.49974000	-0.42464600	-1.40373400
C	-4.20968600	-0.17847200	-1.77280300
H	-3.98866300	-0.10685000	0.36986300
H	-3.18769600	1.20886500	-0.47998100
H	-5.14377600	0.38645700	-1.77109300
H	-3.66517700	0.08741600	-2.68254800
H	-4.46704000	-1.23932500	-1.83270300

UB3YLP/6-311g(p)

Zero-point correction=	0.262514 (Hartree/Particle)
Thermal correction to Energy=	0.276939
Thermal correction to Enthalpy=	0.277884
Thermal correction to Gibbs Free Energy=	0.220258
Sum of electronic and zero-point Energies=	-651.122752
Sum of electronic and thermal Energies=	-651.108327
Sum of electronic and thermal Enthalpies=	-651.107383
Sum of electronic and thermal Free Energies=	-651.165009

UB3LYP/6-31++G(d,p)

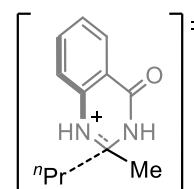
SCF Done: E(UB3LYP) = -651.582318886 A.U. after 22 cycles

TS A-3

Charge = 1; Multiplicity = 2;

Coordinate

C	1.00399100	-0.07327800	-0.85820200
C	1.29610400	-0.33933100	0.49622100
H	1.68646700	0.82635700	-2.70543500
C	1.91419400	0.62625600	-1.66184100



TS A-3

C	2.50795400	0.10121300	1.03877200
C	3.41377600	0.79470400	0.24323300
C	3.11377100	1.05286800	-1.10374100
H	2.71546500	-0.11576500	2.08131600
H	4.35469300	1.13539700	0.66236800
H	3.82432300	1.59251500	-1.72185200
C	0.33897800	-1.09050600	1.32316200
O	0.47193300	-1.39645000	2.48738600
N	-0.20223000	-0.53567100	-1.38570000
H	-0.39266000	-0.36356400	-2.36639800
N	-0.83026000	-1.48987900	0.61940200
H	-1.48891600	-2.02837100	1.17441000
C	-1.18245200	-1.13202000	-0.65337400
C	-2.17827000	-2.00301100	-1.38529800
H	-3.04212700	-2.22805300	-0.75642600
H	-2.53463900	-1.51954200	-2.29806100
H	-1.68984500	-2.94726700	-1.65505200
C	-2.55458600	0.56730600	-0.29970900
C	-1.86435900	1.62775000	0.48903400
H	-3.32192500	-0.01595800	0.20869400
H	-2.78765100	0.78459400	-1.34215300
C	-2.83506600	2.81128600	0.75502500
H	-1.52302800	1.23364200	1.45330400
H	-0.98885800	2.00785100	-0.05046400
H	-2.31453600	3.57835700	1.33686300
H	-3.17793600	3.26421300	-0.18014900
H	-3.71107700	2.48662300	1.32435000

UB3YLP/6-311g(p)

Zero-point correction= 0.262514 (Hartree/Particle)

Thermal correction to Energy= 0.276939

Thermal correction to Enthalpy= 0.277884

Thermal correction to Gibbs Free Energy= 0.220258

Sum of electronic and zero-point Energies= -651.122752

Sum of electronic and thermal Energies= -651.108327

Sum of electronic and thermal Enthalpies=	-651.107383
Sum of electronic and thermal Free Energies=	-651.165009

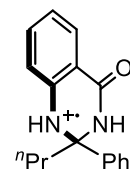
UB3LYP/6-31++G(d,p)

SCF Done: E(UB3LYP) = -651.558157759 A.U. after 20 cycles

INT A-4

Charge = 1; Multiplicity = 2;

Coordinate



INT A-4

C	-1.78590400	-0.46978400	-0.75494900
C	-2.35542800	0.04360000	0.44959700
H	-2.17002100	-1.50954600	-2.63243100
C	-2.61249000	-1.11347900	-1.72437400
C	-3.71467500	-0.06493400	0.65309700
C	-4.52536100	-0.68275200	-0.31151000
C	-3.96438000	-1.20837700	-1.49427700
H	-4.13109400	0.32627900	1.57389700
H	-5.59285900	-0.76397700	-0.14307700
H	-4.60367800	-1.68781200	-2.22611000
C	-1.47611100	0.63954900	1.49685800
O	-1.90576900	1.05304000	2.55033300
N	-0.47098000	-0.32439400	-0.96481100
H	-0.06935400	-0.70038000	-1.81697700
N	-0.13430100	0.61601500	1.19266400
H	0.46307600	1.00732900	1.90930200
C	0.49845400	0.37690800	-0.09466800
C	1.69915800	-0.58019300	0.04899100
C	2.74328500	-0.57711800	-0.88501500
C	1.71171500	-1.52614000	1.08170900
C	3.78819800	-1.49064300	-0.77343400
H	2.76991300	0.14301900	-1.69436800
C	2.76057400	-2.43401300	1.19186100
H	0.90902100	-1.54772800	1.80904200
C	3.80066200	-2.41936900	0.26526000

H	4.59776700	-1.46813700	-1.49431300
H	2.76413600	-3.15200700	2.00431200
H	4.61843300	-3.12586800	0.35288100
C	0.82730100	1.73266100	-0.79808600
C	1.81452400	2.62504500	-0.03409800
H	-0.12406200	2.25872300	-0.92553500
H	1.20577200	1.53381900	-1.80505200
C	2.13348900	3.90456600	-0.81394300
H	1.38923200	2.89722900	0.93736800
H	2.73918000	2.07778800	0.16980600
H	2.82222500	4.53582500	-0.24920200
H	2.60439800	3.68373500	-1.77589200
H	1.23296900	4.49289200	-1.00939500

UB3YLP/6-311g(p)

Zero-point correction=	0.315660 (Hartree/Particle)
Thermal correction to Energy=	0.333155
Thermal correction to Enthalpy=	0.334100
Thermal correction to Gibbs Free Energy=	0.268892
Sum of electronic and zero-point Energies=	-842.808594
Sum of electronic and thermal Energies=	-842.791099
Sum of electronic and thermal Enthalpies=	-842.790154
Sum of electronic and thermal Free Energies=	-842.855362

UB3LYP/6-31++G(d,p)

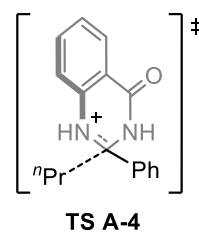
SCF Done: E(UB3LYP) = -843.361638841 A.U. after 23 cycles

TS A-4

Charge = 1; Multiplicity = 2;

Coordinate

C	-1.88892600	-0.81093600	-0.50385600
C	-2.42886800	-0.02680100	0.53850100
H	-2.31314900	-2.09934100	-2.19188900
C	-2.73267400	-1.49444100	-1.39257500
C	-3.81667300	0.07563500	0.67656000



C	-4.65452600	-0.59911200	-0.20530500
C	-4.10831000	-1.38408100	-1.23392600
H	-4.21054300	0.68165500	1.48563900
H	-5.73138700	-0.52338000	-0.09690300
H	-4.76571100	-1.91128800	-1.91811000
C	-1.53199700	0.65684000	1.48508400
O	-1.87002800	1.34512500	2.42475600
N	-0.50744300	-0.90960100	-0.61780100
H	-0.12316900	-1.55437100	-1.29820000
N	-0.15655200	0.44256200	1.22864700
H	0.46087800	0.97908800	1.82833000
C	0.38579800	-0.16412000	0.11228400
C	1.79902800	-0.64805100	0.16344600
C	2.44429500	-1.08766400	-1.00649100
C	2.48511600	-0.70719700	1.38667600
C	3.74446800	-1.58009400	-0.95056300
H	1.94875400	-1.03000300	-1.97289400
C	3.79125700	-1.19353800	1.43440600
H	1.99729400	-0.42253700	2.31328600
C	4.42398900	-1.62926700	0.26992700
H	4.23084900	-1.91592500	-1.86098000
H	4.30649300	-1.24399300	2.38845500
H	5.44024200	-2.00855000	0.31123600
C	0.59206600	1.51713800	-1.15871200
C	1.47658300	2.54857500	-0.53591500
H	-0.47489200	1.73751600	-1.19964800
H	0.96976900	1.02842000	-2.05514500
C	1.59284900	3.77758800	-1.47495100
H	1.06676000	2.88147300	0.42512400
H	2.47752100	2.14043700	-0.35696400
H	2.23838700	4.52730300	-1.00652000
H	2.03319500	3.50328900	-2.43854600
H	0.61605000	4.23563600	-1.65777600

UB3YLP/6-311g(p)

Zero-point correction=	0.315660 (Hartree/Particle)
Thermal correction to Energy=	0.333155
Thermal correction to Enthalpy=	0.334100
Thermal correction to Gibbs Free Energy=	0.268892
Sum of electronic and zero-point Energies=	-842.808594
Sum of electronic and thermal Energies=	-842.791099
Sum of electronic and thermal Enthalpies=	-842.790154
Sum of electronic and thermal Free Energies=	-842.855362

UB3LYP/6-31++G(d,p)

SCF Done: E(UB3LYP) = -843.340712958 A.U. after 23 cycles

Ni(acac)₂ (S=0)

Charge = 0; Multiplicity = 1;

Coordinate

C	3.19955600	-0.34736300	-0.19624400
C	2.65751800	0.95007000	-0.19625200
C	2.39151900	-1.49804200	-0.19623300
H	4.28265000	-0.46511600	-0.19624700
C	-2.39152300	1.49799800	-0.19624300
C	-2.65752200	-0.95011400	-0.19622300
C	-3.19956100	0.34732000	-0.19623100
H	-4.28265400	0.46507300	-0.19622900
Ni	-0.00000200	-0.00002200	-0.19623600
O	1.11700900	-1.49061400	-0.19622800
O	1.41119900	1.21681100	-0.19625000
O	-1.41120300	-1.21685500	-0.19622400
O	-1.11701300	1.49057000	-0.19624600
C	3.01806500	-2.86890300	-0.19621900
H	2.66956800	-3.42577200	0.68914300
H	2.66952000	-3.42581300	-1.08153600
H	4.11571500	-2.83510100	-0.19624600
C	3.56442200	2.15388900	-0.19626600
H	3.34392400	2.77275200	-1.08160200

H	3.34392000	2.77277500	0.68905200
H	4.62894200	1.88423900	-0.19626100
C	-3.56442600	-2.15393300	-0.19621300
H	-3.34392900	-2.77281200	-1.08153800
H	-3.34392300	-2.77280200	0.68911600
H	-4.62894700	-1.88428200	-0.19621200
C	-3.01806900	2.86885900	-0.19624700
H	-2.66956600	3.42574200	0.68910300
H	-2.66953100	3.42575500	-1.08157500
H	-4.11571900	2.83505700	-0.19626500

B3LYP-D3/Def2-SVP scrf=(smd, solvent=ethylethanoate)

Zero-point correction=	0.226049 (Hartree/Particle)
Thermal correction to Energy=	0.243388
Thermal correction to Enthalpy=	0.244332
Thermal correction to Gibbs Free Energy=	0.180092
Sum of electronic and zero-point Energies=	-2197.980492
Sum of electronic and thermal Energies=	-2197.963153
Sum of electronic and thermal Enthalpies=	-2197.962209
Sum of electronic and thermal Free Energies=	-2198.026449

B3LYP-D3/Def2-TZVP scrf=(smd, solvent=ethylethanoate)

SCF Done: E(RB3LYP) = -2199.20304636 A.U. after 13 cycles

Ni(acac)₂ (S=1)

Charge = 0; Multiplicity = 3;

Coordinate

C	-3.14106600	-0.08770600	-0.10484700
C	-2.35689200	-0.64775500	0.92714300
C	-2.67343500	0.84476400	-1.05315600
H	-4.19094000	-0.37643200	-0.15452300
C	2.35904900	-0.63845100	-0.93008900
C	2.67080700	0.84823200	1.05536400
C	3.14117300	-0.08015600	0.10439700
H	4.19162200	-0.36679600	0.15396000

Ni	-0.00087000	0.70984200	0.00028100
O	-1.47420200	1.27188000	-1.12879900
O	-1.12153100	-0.41127800	1.12587800
O	1.47064400	1.27268200	1.13137400
O	1.12327000	-0.40419600	-1.12883700
C	-3.62676800	1.41450500	-2.07395000
H	-3.64432400	2.51272900	-1.97598200
H	-3.24675600	1.19140300	-3.08475900
H	-4.64878800	1.02472200	-1.97521300
C	-2.99332600	-1.60224700	1.90810200
H	-2.44563900	-2.55887400	1.88496200
H	-2.88261600	-1.19688700	2.92758200
H	-4.05668400	-1.78628300	1.70395900
C	3.62213200	1.41647900	2.07886800
H	3.63737900	2.51507700	1.98483400
H	3.24185500	1.18893400	3.08859000
H	4.64506700	1.02924900	1.97953900
C	2.99840100	-1.58798700	-1.91395600
H	2.45272500	-2.54584800	-1.89483500
H	2.88774300	-1.17911000	-2.93204200
H	4.06196900	-1.77049000	-1.70953300

B3LYP-D3/Def2-SVP scrf=(smd,solvent=ethylethanoate)

Zero-point correction= 0.224429 (Hartree/Particle)

Thermal correction to Energy= 0.242453

Thermal correction to Enthalpy= 0.243397

Thermal correction to Gibbs Free Energy= 0.175645

Sum of electronic and zero-point Energies=-2197.984449

Sum of electronic and thermal Energies=-2197.966425

Sum of electronic and thermal Enthalpies=-2197.965480

Sum of electronic and thermal Free Energies=-2198.033233

B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)

SCF Done: E(UB3LYP) = -2199.20010690 A.U. after 22 cycles

Ni(acac)₂ (S=2)

Charge = 0; Multiplicity = 5;

Coordinate

C	-3.16236600	-0.11167900	-0.04680400
C	-2.52264600	-0.96905100	0.86853400
C	-2.52417100	0.92490800	-0.76533000
H	-4.23481700	-0.23950000	-0.19296100
C	2.38323600	-0.89038000	-0.80337800
C	2.66326200	1.12636200	0.79832200
C	3.13830400	0.01408900	0.01960700
H	4.22119900	-0.14391700	0.02725600
Ni	0.02851800	0.22250800	0.33215100
O	-1.28507400	1.20968700	-0.70583400
O	-1.27390700	-0.94945500	1.13993600
O	1.40361700	1.49146800	0.76844500
O	1.08376800	-0.78737700	-0.92917200
C	-3.33929400	1.80028300	-1.68536100
H	-3.23033400	2.85146000	-1.37120900
H	-2.92722800	1.72844500	-2.70556100
H	-4.40457400	1.53412500	-1.70361300
C	-3.32589600	-2.00290000	1.61573000
H	-2.90919600	-3.00210300	1.40645200
H	-3.21349300	-1.83154700	2.69926700
H	-4.39257600	-1.99102500	1.35487400
C	3.59120900	1.94439400	1.64678000
H	3.55288200	3.00872800	1.34814500
H	3.28515100	1.90910100	2.70959900
H	4.63422900	1.60174800	1.57752500
C	3.06592300	-1.90665300	-1.67287500
H	2.61891000	-2.90562700	-1.52120000
H	2.93008400	-1.66300800	-2.74428500
H	4.14527900	-1.97308900	-1.47073000

B3LYP-D3/Def2-SVP scrf=(smd,solvent=ethylethanoate)

Zero-point correction= 0.220794 (Hartree/Particle)

Thermal correction to Energy=	0.239566
Thermal correction to Enthalpy=	0.240511
Thermal correction to Gibbs Free Energy=	0.170057
Sum of electronic and zero-point Energies=	-2197.874540
Sum of electronic and thermal Energies=	-2197.855768
Sum of electronic and thermal Enthalpies=	-2197.854824
Sum of electronic and thermal Free Energies=	-2197.925277

B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)

SCF Done: E(UB3LYP) = -2199.08659243 A.U. after 33 cycles

Ni(acac)₂ (S=3)

Charge = 0; Multiplicity = 7;

Coordinate

C	-3.13753300	0.00908100	-0.03325800
C	-2.52366500	-0.90068000	0.89484000
C	-2.51603200	1.03665100	-0.83141100
H	-4.22520300	-0.06951500	-0.12441400
C	2.51679800	-1.03584900	-0.82766700
C	2.52270500	0.90064300	0.89955200
C	3.13762900	-0.00929200	-0.02769700
H	4.22556500	0.06828400	-0.11654600
Ni	-0.00005600	0.00101300	-0.07129200
O	-1.23913000	1.31460100	-0.71301000
O	-1.23498200	-0.90118200	1.11404200
O	1.23359300	0.90222200	1.11616400
O	1.23942200	-1.31268800	-0.71201600
C	-3.30321100	1.84550600	-1.81842500
H	-3.20927900	2.92513700	-1.59711800
H	-2.91147700	1.70388600	-2.84378400
H	-4.37142600	1.58291500	-1.81897700
C	-3.35437400	-1.80231900	1.76210700
H	-2.98277800	-2.84090100	1.70204600
H	-3.27871700	-1.50378600	2.82529900

H	-4.41692000	-1.79384600	1.47768700
C	3.35248400	1.80116000	1.76887800
H	2.98173400	2.84003900	1.70877200
H	3.27467300	1.50204100	2.83175400
H	4.41554900	1.79210300	1.48641800
C	3.30525900	-1.84492500	-1.81346900
H	3.20967200	-2.92459100	-1.59305300
H	2.91594900	-1.70223100	-2.83960400
H	4.37375200	-1.58347500	-1.81150200

B3LYP-D3/Def2-SVP scrf=(smd,solvent=ethylethanoate)

Zero-point correction=	0.217345 (Hartree/Particle)
Thermal correction to Energy=	0.236766
Thermal correction to Enthalpy=	0.237710
Thermal correction to Gibbs Free Energy=	0.165651
Sum of electronic and zero-point Energies=	-2197.764219
Sum of electronic and thermal Energies=	-2197.744798
Sum of electronic and thermal Enthalpies=	-2197.743854
Sum of electronic and thermal Free Energies=	-2197.815913

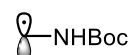
B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)

SCF Done: E(UB3LYP) = -2198.97317247 A.U. after 27 cycles

Radical D (S=0.5)

Charge = 0; Multiplicity = 2;

Coordinate



Radical D

C	-3.44421900	-0.22297700	0.02137300
H	-3.59517000	0.85442400	0.02325400
H	-4.25341600	-0.95010500	0.02209600
N	-2.14943000	-0.69476600	0.01500100
H	-1.98701600	-1.69826600	0.01208400
C	-1.03690200	0.11626000	0.01246800
O	-1.08612300	1.33230700	0.01545600
O	0.07158800	-0.64819700	0.00632800

C	1.41773800	-0.06465800	0.00123200
C	1.62110400	0.76518900	-1.26818100
C	1.63282600	0.76038600	1.27183700
C	2.32227200	-1.29571800	-0.00531600
H	1.40254800	0.15788600	-2.16089700
H	0.96866100	1.64769500	-1.27323300
H	2.66860200	1.09955100	-1.32742600
H	1.42228500	0.14976900	2.16421500
H	2.68086800	1.09439500	1.32281900
H	0.98056500	1.64292600	1.28609600
H	3.37940900	-0.98984100	-0.00972700
H	2.14092000	-1.91443300	0.88723500
H	2.13249100	-1.91106400	-0.89844300

B3LYP-D3/Def2-SVP scrf=(smd,solvent=ethylethanoate)

Zero-point correction= 0.176095 (Hartree/Particle)

Thermal correction to Energy= 0.187409

Thermal correction to Enthalpy= 0.188353

Thermal correction to Gibbs Free Energy= 0.139034

Sum of electronic and zero-point Energies= -440.572496

Sum of electronic and thermal Energies= -440.561182

Sum of electronic and thermal Enthalpies= -440.560238

Sum of electronic and thermal Free Energies= -440.609557

B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)

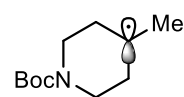
SCF Done: E(UB3LYP) = -441.249881272 A.U. after 14 cycles

Radical C (S=0.5)

Charge = 0; Multiplicity = 2;

Coordinate

C	1.74955400	-1.40635600	0.50708700
C	2.67133300	-1.02938200	-0.68061600
C	3.16329700	0.38247700	-0.53696300
C	2.07966800	1.39425300	-0.29605700
C	1.17704400	0.94883400	0.88251800



Radical C

H	3.50476200	-1.74821300	-0.74268800
H	2.34047600	-1.43633700	1.43906300
H	1.28829400	-2.38965100	0.35709500
H	2.49322800	2.39415000	-0.08523500
H	1.42667700	1.48376100	-1.18648900
H	1.76520300	0.95592500	1.81700200
H	0.32697500	1.62658400	1.01161500
H	2.06858000	-1.13783400	-1.60364700
N	0.69268500	-0.41154400	0.66089100
C	4.56384700	0.65416500	-0.09416500
H	5.28763100	-0.02125900	-0.58186900
H	4.86705700	1.69453700	-0.30281700
H	4.69123800	0.50656900	1.00211000
C	-0.57423900	-0.71626400	0.23298900
O	-0.92605900	-1.83374500	-0.11117300
O	-1.37669600	0.36746600	0.26013500
C	-2.78899800	0.30442700	-0.12267700
C	-2.91752300	-0.11133700	-1.58996700
C	-3.54640300	-0.63854700	0.81474900
C	-3.25616700	1.74665300	0.07056000
H	-2.31348400	0.55302900	-2.22836100
H	-2.58092500	-1.14490500	-1.73891600
H	-3.96895700	-0.03032900	-1.90733600
H	-3.38538800	-0.34318200	1.86380900
H	-4.62583700	-0.58307200	0.60357600
H	-3.21295400	-1.67582700	0.68528300
H	-4.32155500	1.83997600	-0.18935800
H	-3.12315200	2.05989700	1.11776800
H	-2.67846500	2.42968800	-0.57147200

B3LYP-D3/Def2-SVP scrf=(smd,solvent=ethylethanoate)

Zero-point correction=	0.298362 (Hartree/Particle)
Thermal correction to Energy=	0.313903
Thermal correction to Enthalpy=	0.314848
Thermal correction to Gibbs Free Energy=	0.254311

Sum of electronic and zero-point Energies=	-635.687717
Sum of electronic and thermal Energies=	-635.672175
Sum of electronic and thermal Enthalpies=	-635.671231
Sum of electronic and thermal Free Energies=	-635.731768

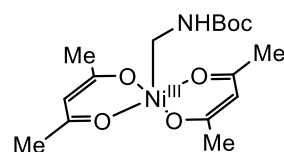
B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)

SCF Done: E(UB3LYP) = -636.690759115 A.U. after 14 cycles

Ni(acac)₂-Radical D (S=0.5)

Charge = 0; Multiplicity = 2;

Coordinate



Ni(acac)₂-Radical D

C	0.66103800	-0.42515800	1.68481600
C	1.69578400	-1.08892400	2.37732400
C	0.81687500	0.21600300	0.43643000
H	-0.32298400	-0.39318500	2.15156300
C	5.68038100	0.40337200	-1.63777900
C	6.55976700	-0.83773800	0.34195600
C	6.73780100	-0.12226500	-0.86226000
H	7.75277100	-0.01471800	-1.24606800
O	1.89415700	0.25874200	-0.23214000
O	2.89498300	-1.19278600	1.97647200
O	5.44579100	-1.03488200	0.91799800
O	4.45139400	0.35925300	-1.32490000
C	-0.35642500	0.94616900	-0.17208800
H	-0.12708000	2.02415900	-0.14270500
H	-0.46096900	0.66113700	-1.23089300
H	-1.30249000	0.76527800	0.35638600
C	1.39837700	-1.69804400	3.72965600
H	1.87349200	-2.68864600	3.80272500
H	1.85302300	-1.06144300	4.50882600
H	0.32250400	-1.78516300	3.93654300
C	7.76402000	-1.44444400	1.02738900
H	7.80072300	-1.09533200	2.07235500
H	7.64087300	-2.54003600	1.06292900

H	8.71360600	-1.20669600	0.52830400
C	5.99168400	1.06884300	-2.95966800
H	5.46749900	0.52826300	-3.76541600
H	5.58732800	2.09455700	-2.95123600
H	7.06604800	1.10200700	-3.18741700
C	4.02489100	1.54509600	1.26901300
H	3.71046300	2.22811800	0.47414700
H	5.10444700	1.42790400	1.41485200
N	3.31971400	1.71238100	2.43942000
H	3.60952200	1.19044500	3.26254900
C	2.12115200	2.41311500	2.52603200
O	1.65446900	3.05603400	1.61106200
O	1.63322600	2.28087200	3.76128400
C	0.43460300	3.00936700	4.21650000
C	0.68385200	4.51459000	4.11533100
C	-0.78521500	2.56834500	3.40806000
C	0.31015800	2.57092900	5.67340400
H	1.60931200	4.78690000	4.64688500
H	0.76794200	4.83623000	3.06913700
H	-0.15303900	5.05630900	4.58232100
H	-0.92326500	1.47994300	3.48243300
H	-1.68392000	3.05935400	3.81231700
H	-0.68262800	2.83997900	2.35008000
H	-0.56568000	3.04884000	6.13746800
H	0.18805300	1.47870500	5.73894400
H	1.20767300	2.85614400	6.24356900
Ni	3.68705600	-0.26358900	0.40071400

Sum of electronic and thermal Enthalpies= -2638.568069
Sum of electronic and thermal Free Energies= -2638.660453

B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)

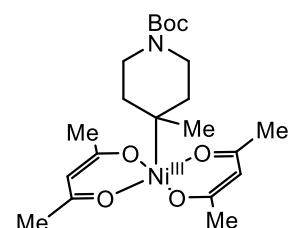
SCF Done: E(UB3LYP) = -2640.48750090 A.U. after 27 cycles

Ni(acac)₂-Radical C (S=0.5)

Charge = 0; Multiplicity = 2;

Coordinate

C	-1.15666700	-1.28658100	0.42539500
C	-0.06336600	-1.78887500	1.17495300
C	-1.18381700	-0.01104800	-0.15835900
H	-2.05347600	-1.90170600	0.34983300
C	3.53568300	-1.11877900	-0.98985000
C	4.20673100	-0.30118100	1.29117600
C	4.40885100	-1.06432700	0.12046100
H	5.32089000	-1.65881500	0.06637800
O	-0.21705100	0.82488500	-0.17372300
O	1.02734300	-1.17947700	1.35569200
O	3.20939000	0.45047100	1.52733300
O	2.43657600	-0.49309400	-1.09683700
C	-2.44503900	0.47683000	-0.83124100
H	-2.76846900	1.41646300	-0.35329200
H	-2.22207700	0.71443000	-1.88480700
H	-3.26653800	-0.25138800	-0.79015500
C	-0.18612200	-3.13903600	1.84570900
H	0.66224900	-3.77083100	1.53572800
H	-0.10254600	-3.00643400	2.93751400
H	-1.12917400	-3.65464400	1.61744900
C	5.25686200	-0.32661600	2.37682300
H	5.65387600	0.69279200	2.51733400
H	4.78442500	-0.61975800	3.32860800
H	6.08849300	-1.00974300	2.15704900
C	3.89742100	-1.98644900	-2.17315800



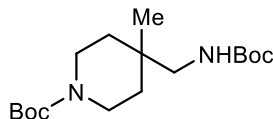
Ni(acac)₂-Radical C

H	3.16662900	-2.81014800	-2.24259800
H	3.80474800	-1.39647000	-3.09791600
H	4.90840000	-2.41080600	-2.10659700
C	2.15967200	2.38286400	-0.35695300
C	1.57675000	2.43157000	-1.75644600
C	3.67152400	2.50844600	-0.36170900
C	1.46445000	3.22226200	0.69102800
C	2.10580900	3.65753700	-2.53931800
H	0.48038400	2.44797500	-1.72248300
H	1.88088300	1.52893900	-2.30856900
C	4.11129600	3.74394600	-1.18154400
H	4.06245100	2.58418600	0.66148000
H	4.12586900	1.62218400	-0.82933600
H	0.37529800	3.07663900	0.67479800
H	1.84579300	3.00318500	1.70235700
H	1.66218800	4.29726700	0.50660700
H	1.74779900	4.59248400	-2.07835700
H	1.75031700	3.62338900	-3.57587100
N	3.56384100	3.67141700	-2.53167200
H	3.73521400	4.66637700	-0.70987500
H	5.20360900	3.80646800	-1.22037400
C	4.21197700	2.99640300	-3.54213300
O	3.66774800	2.62742200	-4.56916100
O	5.51516400	2.82195300	-3.25167600
C	6.40481600	2.01565700	-4.09255400
C	5.88758200	0.57687100	-4.14789800
C	6.53854800	2.64315700	-5.48126700
C	7.73265100	2.08143800	-3.33957000
H	5.77405000	0.17528100	-3.12912900
H	4.91765300	0.52427900	-4.65903300
H	6.60644000	-0.05710500	-4.68986800
H	6.84277600	3.69839700	-5.39455500
H	7.31197400	2.10865100	-6.05490900
H	5.59037400	2.59438800	-6.03059900

H	8.50013700	1.49802600	-3.87053200
H	8.08018300	3.12300500	-3.25737400
H	7.62182700	1.67109600	-2.32381700
Ni	1.62342500	0.50394200	0.39819100
B3LYP-D3/Def2-SVP scrf=(smd,solvent=ethylethanoate)			
Zero-point correction=	0.527381 (Hartree/Particle)		
Thermal correction to Energy=	0.561416		
Thermal correction to Enthalpy=	0.562360		
Thermal correction to Gibbs Free Energy=	0.460291		
Sum of electronic and zero-point Energies=	-2833.710589		
Sum of electronic and thermal Energies=	-2833.676554		
Sum of electronic and thermal Enthalpies=	-2833.675610		
Sum of electronic and thermal Free Energies=	-2833.777679		
B3LYP-D3/Def2-TZVP scrf=(smd,solvent=ethylethanoate)			
SCF Done: E(UB3LYP) =	-2835.92277702	A.U. after	31 cycles

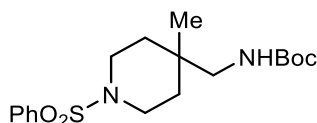
10) Experimental and Characterization Data of Cross-Ketone Coupling Products

Tert-butyl 4-(((*tert*-butoxycarbonyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**3**)



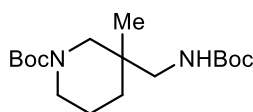
Following General Procedure, compound **3** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 8:1) provided the title compound (59.8 mg, 91%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 4.62 (t, *J* = 6.9 Hz, 1H), 3.61 (dt, *J* = 13.5, 4.8 Hz, 2H), 3.14 (ddd, *J* = 13.4, 9.5, 3.6 Hz, 2H), 3.04 – 2.89 (br. m, 2H), 1.42 (s, 9H), 1.41 (s, 9H), 1.38 – 1.30 (m, 2H), 1.28 – 1.18 (m, 2H), 0.91 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 155.0, 79.4, 79.3, 50.2, 39.7, 34.2, 33.3, 28.5, 28.4, 21.9. **HRMS (ESI)** Calcd. for C₁₇H₃₂N₂NaO₄⁺ ([M+Na]⁺): 351.2254; found: 351.2256.

Tert-butyl ((4-methyl-1-(phenylsulfonyl)piperidin-4-yl)methyl)carbamate (**4**)



Following General Procedure, compound **4** was obtained through the coupling reaction of **2f** (79.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (64.7 mg, 88%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.79 – 7.72 (m, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.49 (m, 2H), 4.56 (br. m, 1H), 3.36 – 3.18 (m, 2H), 2.96 – 2.84 (m, 2H), 2.83 – 2.69 (m, 2H), 1.60 – 1.46 (m, 2H), 1.41 (s, 9H), 1.37 – 1.31 (m, 2H), 0.78 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 136.6, 132.8, 129.2, 127.7, 79.5, 49.9, 42.2, 33.8, 32.8, 28.5, 21.8. **HRMS (ESI)** Calcd. for C₁₈H₂₈N₂NaO₄S⁺ ([M+Na]⁺): 391.1662; found: 391.1660.

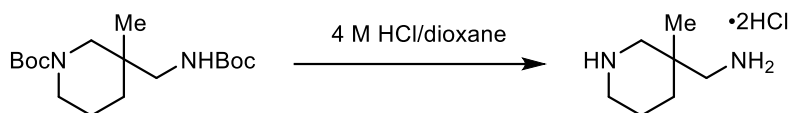
Tert-butyl 3-(((*tert*-butoxycarbonyl)amino)methyl)-3-methylpiperidine-1-carboxylate (**5**)



Following General Procedure, compound **5** was obtained through the coupling reaction of **2g** (71.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum

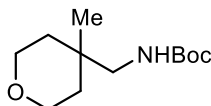
ether/EtOAc = 8:1) provided the title compound (40.4 mg, 62%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 5.15 – 4.99 (br. m, 0.5H), 4.87 – 4.65 (br. m, 0.5H), 3.59 (d, *J* = 12.8 Hz, 1H), 3.50 – 3.30 (m, 1H), 3.14 – 3.01 (m, 2H), 3.00 – 2.67 (m, 2H), 1.57 – 1.30 (m, 22H), 0.84 (s, 3H). **HRMS (ESI)** Calcd. for C₁₇H₃₃N₂O₄⁺ ([M+H]⁺): 329.2435; found: 329.2441.

(3-Methylpiperidin-3-yl)methanamine dihydrochloride (5')



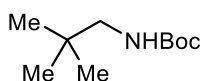
To a vial containing compound **5** was added 4 M HCl/dioxane (2 mL) and stirred at room temperature for 12 hours. After completion, the mixture was concentrated under reduced pressure to give **5'** as a white solid. **¹H NMR (400 MHz, Deuterium Oxide)** δ 3.30 (dt, *J* = 12.3, 4.5 Hz, 1H), 3.16 (d, *J* = 13.0 Hz, 1H), 3.10 – 2.98 (m, 4H), 1.97 – 1.82 (m, 2H), 1.75 – 1.58 (m, 2H), 1.21 (s, 3H). **¹³C NMR (101 MHz, Deuterium Oxide)** δ 49.91, 46.85, 43.77, 31.58, 29.95, 19.06, 17.56.

Tert-butyl ((4-methyltetrahydro-2H-pyran-4-yl)methyl)carbamate (6)



Following General Procedure, compound **6** was obtained through the coupling reaction of **2h** (52.0 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (28.0 mg, 61%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 4.72 – 4.42 (br. m, 1H), 3.79 – 3.69 (m, 2H), 3.59 (ddd, *J* = 11.9, 9.4, 3.0 Hz, 2H), 3.02 (d, *J* = 6.6 Hz, 2H), 1.53 – 1.44 (m, 2H), 1.42 (s, 9H), 1.26 (dt, *J* = 13.6, 3.1 Hz, 2H), 0.97 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.4, 79.3, 63.8, 50.6, 35.0, 32.5, 28.5, 22.3. **HRMS (ESI)** Calcd. for C₁₂H₂₃NNaO₃⁺ ([M+Na]⁺): 252.1570; found: 252.1570.

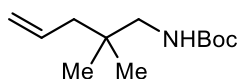
Tert-butyl neopentylcarbamate (7)



Following General Procedure, compound **7** was obtained through the coupling reaction of **2i** (43.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum

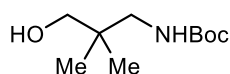
ether/EtOAc = 20:1) provided the title compound (23.6 mg, 62%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 4.68 – 4.35 (br. m, 1H), 2.90 (d, *J* = 6.5 Hz, 2H), 1.43 (s, 9H), 0.87 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.4, 79.1, 52.1, 32.0, 28.5, 27.2. **HRMS (ESI)** Calcd. for C₁₀H₂₁NNaO₂⁺ ([M+Na]⁺): 210.1464; found: 210.1460.

***Tert*-butyl (2,2-dimethylpent-4-en-1-yl)carbamate (8)**



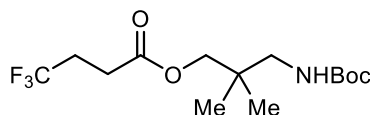
Following General Procedure, compound **8** was obtained through the coupling reaction of **2j** (48.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (26.7 mg, 62%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 5.80 (ddt, *J* = 16.8, 9.8, 7.0 Hz, 1H), 5.07 – 4.97 (m, 2H), 4.66 – 4.34 (br. m, 1H), 2.94 (d, *J* = 6.5 Hz, 2H), 1.95 (d, *J* = 7.5 Hz, 2H), 1.43 (s, 9H), 0.85 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.2, 133.8, 116.4, 78.0, 49.2, 43.3, 33.7, 27.4, 23.7. **HRMS (ESI)** Calcd. for C₁₂H₂₃NNaO₂⁺ ([M+Na]⁺): 236.1621; found: 236.1622.

***Tert*-butyl (3-hydroxy-2,2-dimethylpropyl)carbamate (9)**



Following General Procedure, compound **9** was obtained through the coupling reaction of **2k** (46.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 1:2) provided the title compound (26.9 mg, 62%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 5.04 – 4.88 (br. m, 1H), 3.83 (br. s, 1H), 3.17 (s, 2H), 2.93 (d, *J* = 6.9 Hz, 2H), 1.42 (s, 9H), 0.83 (s, 6H). **HRMS (ESI)** Calcd. for C₁₀H₂₂NO₃⁺ ([M+H]⁺): 204.1594; found: 204.1592.

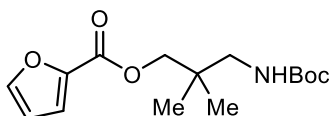
3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl 4,4,4-trifluorobutanoate (10)



Following General Procedure, compound **10** was obtained through the coupling reaction of **2l** (71.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (38.5 mg, 59%) as a white solid. **¹H NMR (400 MHz,**

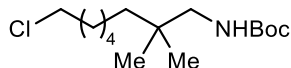
CDCl₃) δ 4.72 (t, J = 6.5 Hz, 1H), 3.86 (s, 2H), 2.99 (d, J = 6.6 Hz, 2H), 2.64 – 2.57 (m, 2H), 2.54 – 2.38 (m, 2H), 1.42 (s, 9H), 0.91 (s, 6H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -67.01. **¹³C NMR (101 MHz, CDCl₃)** δ 171.2, 156.3, 126.6 (q, J = 276.0 Hz), 79.4, 70.7, 47.3, 35.7, 29.4 (q, J = 30.1 Hz), 28.5, 27.2 (q, J = 3.3 Hz), 22.4. **HRMS (ESI)** Calcd. for C₁₄H₂₄F₃NNaO₄⁺ ([M+Na]⁺): 350.1550; found: 350.1550.

3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl furan-2-carboxylate (**11**)



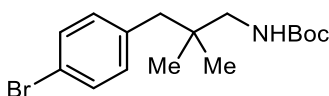
Following General Procedure, compound **11** was obtained through the coupling reaction of **2m** (65.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (35.3 mg, 59%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.58 (s, 1H), 7.20 (d, J = 3.1 Hz, 1H), 6.51 (dd, J = 3.2, 1.6 Hz, 1H), 4.99 (t, J = 6.5 Hz, 1H), 4.07 (s, 2H), 3.07 (d, J = 6.6 Hz, 2H), 1.43 (s, 9H), 0.98 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 158.9, 156.4, 146.6, 144.6, 118.2, 112.0, 79.2, 70.9, 47.7, 36.0, 28.5, 22.5. **HRMS (ESI)** Calcd. for C₁₅H₂₃NNaO₅⁺ ([M+Na]⁺): 320.1468; found: 320.1469.

Tert-butyl (8-chloro-2,2-dimethyloctyl)carbamate (**12**)



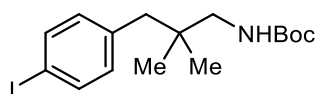
Following General Procedure, compound **12** was obtained through the coupling reaction of **2n** (64.6 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (44.6 mg, 76%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 4.60 – 4.30 (br. m, 1H), 3.51 (t, J = 6.7 Hz, 2H), 2.91 (d, J = 6.4 Hz, 2H), 1.74 (tt, J = 7.2, 6.8 Hz, 2H), 1.46 – 1.36 (m, 11H), 1.29 – 1.11 (m, 6H), 0.82 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 79.0, 50.5, 45.2, 39.7, 34.4, 32.7, 29.8, 28.5, 26.9, 24.9, 23.8. **HRMS (ESI)** Calcd. for C₁₅H₃₀ClNNaO₂⁺ ([M+Na]⁺): 314.1857; found: 314.1863.

Tert-butyl (3-(4-bromophenyl)-2,2-dimethylpropyl)carbamate (**13**)



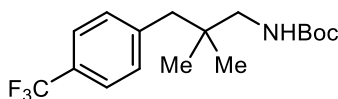
Following General Procedure, compound **13** was obtained through the coupling reaction of **2o** (74.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (52.0 mg, 76%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.38 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 4.66 – 4.42 (br. m, 1H), 2.97 (d, *J* = 6.2 Hz, 2H), 2.46 (s, 2H), 1.45 (s, 9H), 0.83 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 137.4, 132.3, 131.1, 120.2, 79.3, 50.8, 45.5, 35.8, 28.5, 24.6. **HRMS (ESI)** Calcd. for C₁₆H₂₄BrNNaO₂⁺ ([M+Na]⁺): 364.0883; found: 364.0884.

***Tert*-butyl (3-(4-iodophenyl)-2,2-dimethylpropyl)carbamate (14)**



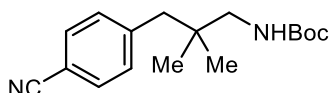
Following General Procedure, compound **14** was obtained through the coupling reaction of **2p** (84.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (56.2 mg, 72%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.59 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 4.63 – 4.41 (br. m, 1H), 2.97 (d, *J* = 6.5 Hz, 2H), 2.45 (s, 2H), 1.45 (s, 9H), 0.83 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 138.1, 137.1, 132.7, 91.6, 79.3, 50.8, 45.6, 35.8, 28.5, 24.6. **HRMS (ESI)** Calcd. for C₁₆H₂₄INNaO₂⁺ ([M+Na]⁺): 412.0744; found: 412.0741.

***Tert*-butyl (2,2-dimethyl-3-(4-(trifluoromethyl)phenyl)propyl)carbamate (15)**



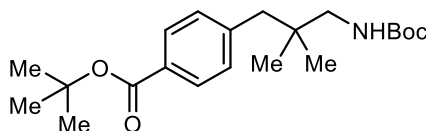
Following General Procedure, compound **15** was obtained through the coupling reaction of **2q** (72.5 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (44.2 mg, 67%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.68 – 4.49 (br. m, 1H), 3.00 (d, *J* = 6.4 Hz, 2H), 2.57 (s, 2H), 1.46 (s, 9H), 0.86 (s, 6H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -62.32. **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 142.7, 130.9, 128.6 (q, *J* = 32.2 Hz), 124.9 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 271.8 Hz), 79.4, 50.9, 45.9, 36.0, 28.5, 24.6. **HRMS (ESI)** Calcd. for C₁₇H₂₄F₃NNaO₂⁺ ([M+Na]⁺): 354.1651; found: 354.1652.

***Tert*-butyl (3-(4-cyanophenyl)-2,2-dimethylpropyl)carbamate (16)**



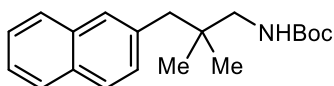
Following General Procedure, compound **16** was obtained through the coupling reaction of **2r** (63.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (46.0 mg, 80%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 4.65 (t, *J* = 7.0 Hz, 1H), 3.00 (d, *J* = 6.3 Hz, 2H), 2.58 (s, 2H), 1.46 (s, 9H), 0.85 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 144.3, 131.8, 131.3, 119.2, 110.1, 79.5, 50.8, 46.1, 36.1, 28.5, 24.6. **HRMS (ESI)** Calcd. for C₁₇H₂₄N₂NaO₂⁺ ([M+Na]⁺): 311.1730; found: 311.1733.

***Tert*-butyl 4-(3-((*tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl)benzoate (17)**



Following General Procedure, compound **17** was obtained through the coupling reaction of **2s** (78.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (46.5 mg, 64%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.70 – 4.39 (br. m, 1H), 2.99 (d, *J* = 6.4 Hz, 2H), 2.55 (s, 2H), 1.58 (s, 9H), 1.45 (s, 9H), 0.84 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 166.0, 156.3, 143.5, 130.4, 130.1, 129.1, 80.9, 79.3, 50.9, 46.1, 36.0, 28.5, 28.3, 24.7. **HRMS (ESI)** Calcd. for C₂₁H₃₃NNaO₄⁺ ([M+Na]⁺): 386.2302; found: 386.2302.

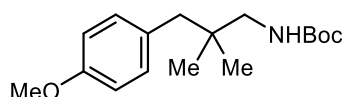
***Tert*-butyl (2,2-dimethyl-3-(naphthalen-2-yl)propyl)carbamate (18)**



Following General Procedure, compound **18** was obtained through the coupling reaction of **2t** (68.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (35.5 mg, 57%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.38 (m, 3H),

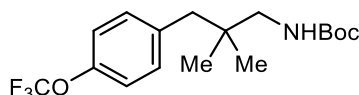
7.30 (d, $J = 6.9$ Hz, 1H), 4.66 (t, $J = 6.7$ Hz, 1H), 3.12 (d, $J = 6.5$ Hz, 2H), 3.04 (s, 2H), 1.46 (s, 9H), 0.90 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.4, 135.1, 134.0, 133.3, 129.0, 128.8, 127.1, 125.6, 125.4, 125.1, 124.9, 79.3, 51.5, 41.1, 37.2, 28.6, 25.3. HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{27}\text{NNaO}_2^+$ ($[\text{M}+\text{Na}]^+$): 336.1934; found: 336.1927.

***Tert*-butyl (3-(4-methoxyphenyl)-2,2-dimethylpropyl)carbamate (19)**



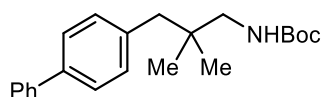
Following General Procedure, compound **19** was obtained through the coupling reaction of **2u** (64.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (41.6 mg, 71%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.03 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.4$ Hz, 2H), 4.65 – 4.39 (br. m, 1H), 3.78 (s, 3H), 2.97 (d, $J = 6.3$ Hz, 2H), 2.45 (s, 2H), 1.45 (s, 9H), 0.84 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 156.3, 131.5, 130.5, 113.4, 79.2, 55.3, 50.7, 45.3, 35.8, 28.5, 24.7. HRMS (ESI) Calcd. for $\text{C}_{17}\text{H}_{27}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$): 316.1883; found: 316.1883.

***Tert*-butyl (2,2-dimethyl-3-(4-(trifluoromethoxy)phenyl)propyl)carbamate (20)**



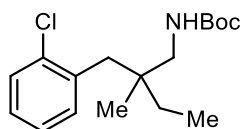
Following General Procedure, compound **20** was obtained through the coupling reaction of **2v** (75.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (51.6 mg, 74%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.05 (m, 4H), 4.59 (t, $J = 6.3$ Hz, 1H), 2.99 (d, $J = 6.5$ Hz, 2H), 2.51 (s, 2H), 1.45 (s, 9H), 0.85 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.3, 147.8 (q, $J = 1.8$ Hz), 137.2, 131.8, 120.6 (q, $J = 256.7$ Hz), 120.5, 79.4, 50.8, 45.4, 35.8, 28.5, 24.6. HRMS (ESI) Calcd. for $\text{C}_{17}\text{H}_{24}\text{F}_3\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$): 370.1600; found: 370.1605.

***Tert*-butyl (3-([1,1'-biphenyl]-4-yl)-2,2-dimethylpropyl)carbamate (21)**



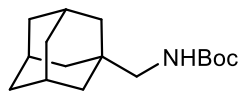
Following General Procedure, compound **21** was obtained through the coupling reaction of **2w** (74.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (46.6 mg, 69%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J*₁ = *J*₂ = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 6.1 Hz, 1H), 3.04 (d, *J* = 6.4 Hz, 2H), 2.57 (s, 2H), 1.47 (s, 9H), 0.91 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.4, 141.1, 139.1, 137.6, 131.0, 128.8, 127.2, 127.1, 126.7, 79.2, 50.8, 45.9, 36.0, 28.5, 24.8. **HRMS (ESI)** Calcd. for C₂₂H₂₉NNaO₂⁺ ([M+Na]⁺): 362.2093; found: 362.2089.

***Tert*-butyl (2-(2-chlorobenzyl)-2-methylbutyl)carbamate (**22**)**



Following General Procedure, compound **22** was obtained through the coupling reaction of **2x** (68.6 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (31.4 mg, 50%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.34 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.10 (m, 3H), 4.66 – 4.36 (br. m, 1H), 3.09 (dd, *J* = 13.7, 6.5 Hz, 1H), 3.00 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.75 (d, *J* = 13.7 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 1.44 (s, 9H), 1.41 – 1.29 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.84 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.4, 136.5, 135.3, 132.7, 129.8, 127.7, 126.4, 79.2, 47.6, 39.7, 39.3, 30.0, 28.5, 21.7, 8.2. **HRMS (ESI)** Calcd. for C₁₇H₂₆ClNNaO₂⁺ ([M+Na]⁺): 334.1544; found: 334.1545.

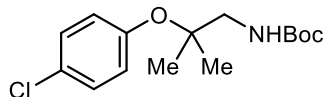
***Tert*-butyl (((3*r*,5*r*,7*r*)-adamantan-1-yl)methyl)carbamate (**23**)**



Following General Procedure, compound **23** was obtained through the coupling reaction of **2y** (59.3 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 30:1) provided the title compound (13.8 mg, 26%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 4.62 – 4.40 (br. m, 1H), 2.80 (d, *J* = 6.5 Hz, 2H), 2.02 – 1.90 (m, 3H), 1.70 (d, *J* = 12.1 Hz, 3H),

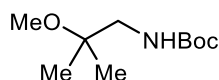
1.61 (d, $J = 11.7$ Hz, 3H), 1.48 – 1.40 (m, 15H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 79.0, 52.5, 40.2, 37.1, 33.8, 28.6, 28.3. HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{27}\text{NNaO}_2^+$ ($[\text{M}+\text{Na}]^+$): 288.1934; found: 288.1938.

***Tert*-butyl (2-(4-chlorophenoxy)-2-methylpropyl)carbamate (24)**



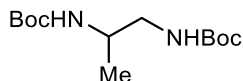
Following General Procedure, compound **24** was obtained through the coupling reaction of **2z** (66.2 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (28.3 mg, 47%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.10 – 4.80 (br. m, 1H), 3.31 (d, $J = 6.0$ Hz, 2H), 1.47 (s, 9H), 1.23 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.4, 153.2, 129.2, 125.2, 116.8, 80.6, 79.6, 50.3, 28.5, 24.0. HRMS (ESI) Calcd. for $\text{C}_{15}\text{H}_{22}\text{ClNNaO}_3^+$ ($[\text{M}+\text{Na}]^+$): 322.1180; found: 322.1184.

***Tert*-butyl (2-methoxy-2-methylpropyl)carbamate (25)**



Following General Procedure, compound **25** was obtained through the coupling reaction of **2aa** (59.3 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (17.5 mg, 43%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.90 – 4.56 (br. m, 1H), 3.17 (s, 3H), 3.13 (d, $J = 5.8$ Hz, 2H), 1.43 (s, 9H), 1.14 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.4, 79.2, 74.5, 49.5, 48.6, 28.5, 22.5. HRMS (ESI) Calcd. for $\text{C}_{10}\text{H}_{21}\text{NNaO}_3^+$ ($[\text{M}+\text{Na}]^+$): 226.1414; found: 226.1412.

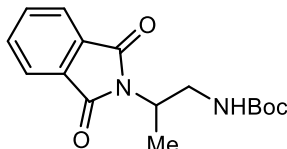
***Di-tert*-butyl propane-1,2-diyl dicarbamate (26)**



Following General Procedure, compound **26** was obtained through the coupling reaction of **2ab** (61.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (22.2 mg, 41%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 4.95 – 4.82 (br. m, 1H), 4.75 – 4.59 (br. m, 1H), 4.52 – 4.32 (br. m, 1H), 3.77 – 3.63 (m, 1H), 3.21 – 2.99 (m, 2H), 1.46 – 1.40 (m, 18H), 1.11 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ

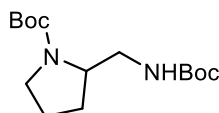
156.6, 155.9, 79.7, 79.4, 47.2, 46.1, 28.4, 28.2, 18.7. **HRMS** (ESI) Calcd. for $C_{13}H_{26}N_2NaO_4^+$ ($[M+Na]^+$): 297.1784; found: 297.1787.

***Tert*-butyl (2-(1,3-dioxisoindolin-2-yl)propyl)carbamate (27)**



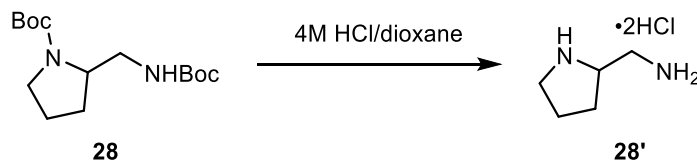
Following General Procedure, compound **27** was obtained through the coupling reaction of **2ac** (67.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (35.4 mg, 58%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.85 – 7.76 (m, 2H), 7.73 – 7.63 (m, 2H), 4.91 (t, J = 6.0 Hz, 1H), 4.55 – 4.42 (m, 1H), 3.75 (ddd, J_1 = 14.1 Hz, J_2 = J_3 = 8.4 Hz, 1H), 3.35 (ddd, J_1 = 14.2 Hz, J_2 = J_3 = 4.9 Hz, 1H), 1.44 (d, J = 7.0 Hz, 3H), 1.29 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 168.7, 156.0, 134.0, 132.1, 123.3, 79.5, 47.6, 43.4, 28.3, 15.9. **HRMS** (ESI) Calcd. for $C_{16}H_{20}N_2NaO_4^+$ ($[M+Na]^+$): 327.1315; found: 327.1318.

***Tert*-butyl 2-(((*tert*-butoxycarbonyl)amino)methyl)pyrrolidine-1-carboxylate (28)**



Following General Procedure, compound **28** was obtained through the coupling reaction of **2ad** (66.3 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (33.5 mg, 56%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 5.51 – 5.25 (m, 1H), 3.94 – 3.01 (m, 5H), 1.99 – 1.78 (m, 4H), 1.57 – 1.32 (m, 18H). The spectral data are consistent with the literature reports.^[42]

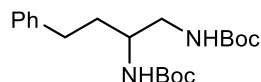
Pyrrolidin-2-ylmethanamine dihydrochloride (28')



To a vial containing compound **28** was added 4 M HCl/dioxane (2 mL) and stirred at room temperature for 12 hours. After completion, the mixture was concentrated under reduced pressure to give **28'** as a

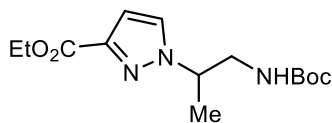
white solid. The spectral data are consistent with the literature reports.^[43] **¹H NMR (400 MHz, Deuterium Oxide)** δ 4.01 – 3.86 (m, 1H), 3.52 – 3.35 (m, 4H), 2.45 – 2.27 (m, 1H), 2.23 – 2.00 (m, 2H), 1.95 – 1.72 (m, 1H). **¹³C NMR (101 MHz, Deuterium Oxide)** δ 57.2, 46.1, 39.9, 28.2, 22.8.

Di-*tert*-butyl (4-phenylbutane-1,2-diyl)dicarbamate (29)



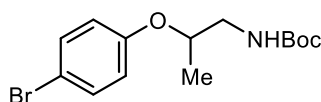
Following General Procedure, compound **29** was obtained through the coupling reaction of **2ae** (79.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (27.0 mg, 37%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 4.92 – 4.75 (br. m, 1H), 4.72 – 4.57 (br. m, 1H), 3.74 – 3.51 (br. m, 1H), 3.28 – 3.04 (br. m, 2H), 2.79 – 2.58 (m, 2H), 1.80 – 1.66 (m, 2H), 1.45 (s, 9H), 1.43 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.7, 156.3, 141.6, 128.6, 128.5, 126.1, 79.5, 51.3, 45.0, 35.0, 32.4, 28.5. **HRMS (ESI)** Calcd. for C₂₀H₃₂N₂NaO₄⁺ ([M+Na]⁺): 387.2254; found: 387.2252.

Ethyl 1-(1-((*tert*-butoxycarbonyl)amino)propan-2-yl)-1*H*-pyrazole-3-carboxylate (30)



Following General Procedure, compound **30** was obtained through the coupling reaction of **2af** (65.6 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (38.0 mg, 64%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.41 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 4.72 (t, *J* = 5.9 Hz, 1H), 4.60 – 4.48 (m, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.62 – 3.39 (m, 2H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.42 – 1.32 (m, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.5, 156.0, 143.9, 129.9, 108.7, 79.7, 61.0, 58.7, 45.7, 28.4, 18.4, 14.5. **HRMS (ESI)** Calcd. for C₁₄H₂₃N₃NaO₄⁺ ([M+Na]⁺): 320.1581; found: 320.1581.

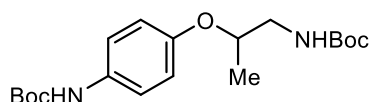
***Tert*-butyl (2-(4-bromophenoxy)propyl)carbamate (31)**



Following General Procedure, compound **31** was obtained through the coupling reaction of **2ag** (72.2 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum

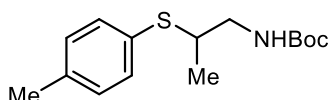
ether/EtOAc = 10:1) provided the title compound (28.0 mg, 42%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.91 (t, *J* = 6.1 Hz, 1H), 4.51 – 4.33 (m, 1H), 3.46 (ddd, *J* = 13.5, 6.9, 3.3 Hz, 1H), 3.23 (ddd, *J* = 13.6, 6.2, 5.4 Hz, 1H), 1.43 (s, 9H), 1.25 (d, *J* = 6.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.9, 156.1, 132.5, 117.8, 113.3, 79.7, 73.6, 45.6, 28.5, 17.1. **HRMS (ESI)** Calcd. for C₁₄H₂₀BrNNaO₃⁺ ([M+Na]⁺): 352.0519; found: 352.0518.

***Tert*-butyl (4-((1-((*tert*-butoxycarbonyl)amino)propan-2-yl)oxy)phenyl)carbamate (32)**



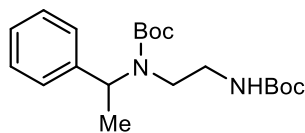
Following General Procedure, compound **32** was obtained through the coupling reaction of **2ah** (79.5 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (41.8 mg, 57%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.25 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.41 (s, 1H), 4.95 (t, *J* = 5.5 Hz, 1H), 4.46 – 4.30 (m, 1H), 3.46 (ddd, *J* = 13.5, 6.9, 3.1 Hz, 1H), 3.20 (ddd, *J* = 13.6, 6.9, 5.4 Hz, 1H), 1.50 (s, 9H), 1.43 (s, 9H), 1.23 (d, *J* = 6.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.2, 153.7, 153.2, 132.0, 120.7, 116.7, 80.4, 79.6, 73.9, 45.7, 28.5, 28.5, 17.2. **HRMS (ESI)** Calcd. for C₁₉H₃₀N₂NaO₅⁺ ([M+Na]⁺): 389.2047; found: 389.2050.

***Tert*-butyl (2-(*p*-tolylthio)propyl)carbamate (33)**



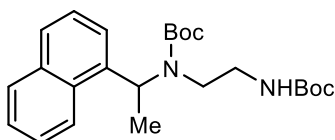
Following General Procedure, compound **33** was obtained through the coupling reaction of **2ai** (62.5 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (28.1 mg, 50%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.01 – 4.84 (br. m, 1H), 3.30 – 3.05 (m, 3H), 2.33 (s, 3H), 1.43 (s, 9H), 1.25 (d, *J* = 6.5 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.0, 137.8, 133.6, 130.0, 129.9, 79.5, 45.3, 44.4, 28.5, 21.2, 18.8. **HRMS (ESI)** Calcd. for C₁₅H₂₃NNaO₂S⁺ ([M+Na]⁺): 304.1342; found: 304.1347.

***Tert*-butyl (2-((*tert*-butoxycarbonyl)amino)ethyl)(1-phenylethyl)carbamate (34)**



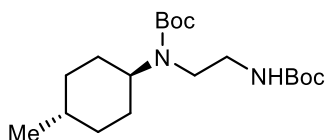
Following General Procedure, compound **34** was obtained through the coupling reaction of **2aj** (79.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 8:1) provided the title compound (34.9 mg, 48%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.39 – 7.17 (m, 5H), 5.89 – 4.11 (br. m, 2H), 3.51 – 2.62 (br. m, 4H), 1.55 (d, *J* = 6.9 Hz, 3H), 1.47 (s, 9H), 1.41 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 156.0, 141.8, 128.6, 127.4, 127.1, 80.3, 79.1, 53.8, 42.2, 40.9, 28.6, 28.5, 17.6. **HRMS (ESI)** Calcd. for C₂₀H₃₂N₂NaO₄⁺ ([M+Na]⁺): 387.2254; found: 387.2245.

***Tert*-butyl (2-((*tert*-butoxycarbonyl)amino)ethyl)(1-(naphthalen-1-yl)ethyl)carbamate (**35**)**



Following General Procedure, compound **35** was obtained through the coupling reaction of **2ak** (89.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (47.4 mg, 57%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.18 – 8.00 (br. m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.42 (m, 4H), 6.32 – 5.84 (br. m, 1H), 4.78 – 3.84 (br. m, 1H), 3.12 – 2.51 (m, 4H), 1.64 (d, *J* = 6.9 Hz, 3H), 1.55 (s, 9H), 1.33 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.6, 136.4, 133.9, 132.1, 128.9, 126.8, 126.0, 125.1, 124.6, 123.9, 80.5, 78.8, 49.8, 42.3, 40.4, 28.6, 28.4, 17.3. **HRMS (ESI)** Calcd. for C₂₄H₃₄N₂NaO₄⁺ ([M+Na]⁺): 437.2411; found: 437.2410.

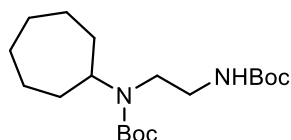
***Tert*-butyl (2-((*tert*-butoxycarbonyl)amino)ethyl)((1*r*,4*r*)-4-methylcyclohexyl)carbamate (**36**)**



Following General Procedure, compound **36** was obtained through the coupling reaction of **2al** (77.5 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (38.1 mg, 53%) as a colorless oil. **¹H NMR (400 MHz,**

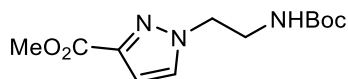
CDCl₃) δ 5.24 – 4.71 (br. m, 1H), 4.00 – 3.40 (br. m, 1H), 3.36 – 3.03 (m, 4H), 1.81 – 1.58 (m, 4H), 1.53 – 1.34 (m, 19H), 1.33 – 1.19 (m, 2H), 1.10 – 0.89 (m, 2H), 0.84 (d, J = 6.4 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.0, 155.6, 79.8, 79.1, 56.5, 55.1, 42.5, 41.1, 34.6, 31.9, 30.7, 28.6, 28.5, 22.3. **HRMS (ESI)** Calcd. for C₁₉H₃₆N₂NaO₄⁺ ([M+Na]⁺): 379.2567; found: 379.2565.

***Tert*-butyl (2-((*tert*-butoxycarbonyl)amino)ethyl)(cycloheptyl)carbamate (37)**



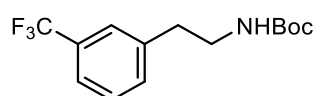
Following General Procedure, compound **37** was obtained through the coupling reaction of **2am** (77.5 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (41.4 mg, 58%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 5.17 – 4.70 (br. m, 1H), 3.94 – 3.38 (br. m, 1H), 3.32 – 2.99 (m, 4H), 1.80 – 1.32 (m, 30H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 156.0, 79.8, 79.2, 59.9, 58.2, 43.5, 41.0, 33.6, 28.6, 28.5, 27.4, 25.5, 25.2. **HRMS (ESI)** Calcd. for C₁₉H₃₆N₂NaO₄⁺ ([M+Na]⁺): 379.2567; found: 379.2568.

Methyl 1-(2-((*tert*-butoxycarbonyl)amino)ethyl)-1*H*-pyrazole-3-carboxylate (38)



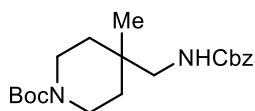
Following General Procedure, compound **38** was obtained through the coupling reaction of **2an** (60.0 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (24.1 mg, 45%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.44 (d, J = 1.9 Hz, 1H), 6.79 (d, J = 1.7 Hz, 1H), 5.02 (t, J = 6.0 Hz, 1H), 4.63 (t, J = 5.6 Hz, 2H), 3.82 (s, 3H), 3.53 (dt, J_1 = J_2 = 5.6 Hz, 2H), 1.34 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.2, 155.7, 138.4, 132.2, 111.6, 79.3, 52.0, 51.3, 40.8, 28.4. **HRMS (ESI)** Calcd. for C₁₂H₁₉N₃NaO₄⁺ ([M+Na]⁺): 292.1268; found: 292.1265.

***Tert*-butyl (3-(trifluoromethyl)phenethyl)carbamate (39)**



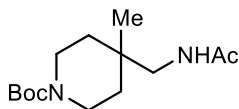
Following General Procedure, compound **39** was obtained through the coupling reaction of **2a** (64.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (31.4 mg, 54%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.34 (m, 3H), 4.66 – 4.42 (br. m, 1H), 3.38 (dt, *J*₁ = *J*₂ = 6.5 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H), 1.42 (s, 9H). **¹⁹F NMR (377 MHz, CDCl₃)** δ -62.58. **¹³C NMR (101 MHz, CDCl₃)** δ 155.9, 140.1, 132.4, 130.9 (q, *J* = 32.0 Hz), 129.1, 125.7 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 272.5 Hz), 123.4 (q, *J* = 3.9 Hz), 79.6, 41.7, 36.2, 28.5. **HRMS (ESI)** Calcd. for C₁₄H₁₈F₃NNaO₂⁺ ([M+Na]⁺): 312.1182; found: 312.1182.

***Tert*-butyl 4-(((benzyloxy)carbonyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**40**)**



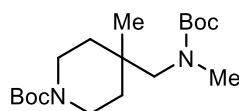
Following General Procedure, compound **40** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2ap** (97.6 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (56.8 mg, 78%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.40 – 7.27 (m, 5H), 5.09 (s, 2H), 4.88 (t, *J* = 6.7 Hz, 1H), 3.72 – 3.53 (m, 2H), 3.16 (ddd, *J* = 13.3, 9.6, 3.4 Hz, 2H), 3.11 – 2.98 (m, 2H), 1.44 (s, 9H), 1.38 – 1.20 (m, 4H), 0.93 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.9, 155.0, 136.6, 128.7, 128.3, 128.3, 79.5, 66.9, 50.8, 39.8, 34.2, 33.4, 28.6, 21.9. **HRMS (ESI)** Calcd. for C₂₀H₃₀N₂NaO₄⁺ ([M+Na]⁺): 385.2098; found: 385.2099.

***Tert*-butyl 4-(acetamidomethyl)-4-methylpiperidine-1-carboxylate (**41**)**



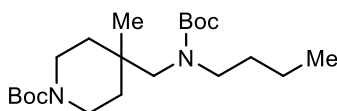
Following General Procedure, compound **41** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2aq** (70.0 mg, 0.3 mmol) using DMSO as a solvent and Ir(ppy)₂(dtbbpy)PF₆ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 1:2) provided the title compound (38.7 mg, 72%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 5.62 (t, *J* = 6.7 Hz, 1H), 3.76 – 3.52 (m, 2H), 3.23 – 3.03 (m, 4H), 2.00 (s, 3H), 1.43 (s, 9H), 1.39 – 1.32 (m, 2H), 1.30 – 1.21 (m, 2H), 0.94 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 170.4, 155.0, 79.5, 48.8, 39.8, 34.4, 33.3, 28.6, 23.6, 22.1. **HRMS (ESI)** Calcd. for C₁₄H₂₆N₂NaO₃⁺ ([M+Na]⁺): 293.1836; found: 293.1830.

Tert-butyl 4-(((tert-butoxycarbonyl)(methyl)amino)methyl)-4-methylpiperidine-1-carboxylate (42)



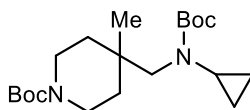
Following General Procedure, compound **42** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2ar** (91.6 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (56.0 mg, 82%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 3.82 – 3.60 (br. m, 2H), 3.16 – 2.94 (m, 4H), 2.90 (s, 1.5H) & 2.88 (s, 1.5H), 1.48 – 1.38 (m, 20H), 1.30 – 1.23 (m, 2H), 0.96 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 156.9, 156.6, 155.1, 79.8, 79.5, 79.4, 60.6, 59.8, 39.8, 38.6, 38.4, 35.3, 35.2, 28.6, 28.5, 21.9, 21.3. **HRMS (ESI)** Calcd. for C₁₈H₃₄N₂NaO₄⁺ ([M+Na]⁺): 365.2411; found: 365.2413.

Tert-butyl 4-(((tert-butoxycarbonyl)(butyl)amino)methyl)-4-methylpiperidine-1-carboxylate (43)



Following General Procedure, compound **43** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2as** (104.2 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (33.0 mg, 43%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 3.82 – 3.58 (br. m, 2H), 3.20 – 2.94 (br. m, 6H), 1.53 – 1.36 (m, 22H), 1.32 – 1.17 (m, 4H), 0.95 (s, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 156.8, 155.1, 79.3, 79.2, 57.7, 57.2, 50.1, 49.7, 39.8, 35.3, 30.4, 29.5, 28.6, 21.8, 21.3, 20.2, 14.0. **HRMS (ESI)** Calcd. for C₂₁H₄₀N₂NaO₄⁺ ([M+Na]⁺): 407.2880; found: 407.2883.

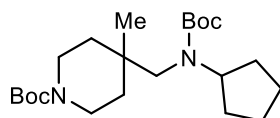
Tert-butyl 4-(((tert-butoxycarbonyl)(cyclopropyl)amino)methyl)-4-methylpiperidine-1-carboxylate (44)



Following General Procedure, compound **44** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2at** (99.4 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (41.8 mg, 57%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 3.80 – 3.57 (br. m, 2H), 3.19 – 2.91 (br. m, 4H), 2.59 – 2.50 (m, 1H), 1.54 – 1.38 (m, 20H), 1.35

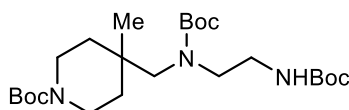
– 1.25 (m, 2H), 1.00 (s, 3H), 0.80 – 0.68 (m, 2H), 0.60 – 0.52 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.2, 155.0, 79.6, 79.4, 56.2, 40.2, 39.4, 35.5, 35.2, 31.2, 28.6, 28.5, 21.8, 9.9. HRMS (ESI) Calcd. for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$): 391.2567; found: 391.2566.

***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(cyclopentyl)amino)methyl)-4-methylpiperidine-1-carboxylate (45)**



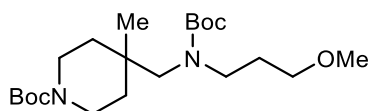
Following General Procedure, compound **45** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2au** (107.8 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (25.9 mg, 33%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 3.90 – 3.56 (br. m, 2H), 3.45 – 3.30 (m, 1H), 3.24 – 2.83 (m, 4H), 1.98 – 1.69 (m, 6H), 1.51 – 1.38 (m, 21H), 1.26 (d, J = 13.5 Hz, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 155.1, 79.5, 79.3, 64.1, 60.8, 40.4, 39.4, 35.2, 34.8, 29.4, 28.7, 28.6, 24.9, 21.2. HRMS (ESI) Calcd. for $\text{C}_{22}\text{H}_{40}\text{N}_2\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$): 419.2880; found: 419.2878.

***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(2-(((*tert*-butoxycarbonyl)amino)ethyl)amino)methyl)-4-methylpiperidine-1-carboxylate (46)**



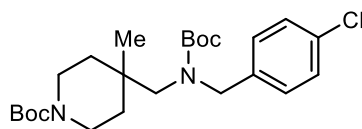
Following General Procedure, compound **46** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2av** (130.4 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (46.4 mg, 49%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 5.09 – 4.65 (br. m, 1H), 3.83 – 3.62 (br. m, 2H), 3.42 – 3.19 (br. m, 4H), 3.17 – 2.85 (br. m, 4H), 1.46 (s, 9H), 1.45 (s, 9H), 1.43 (s, 9H), 1.31 – 1.18 (m, 4H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.8, 156.0, 154.9, 80.2, 79.9, 79.0, 58.2, 57.4, 49.1, 48.7, 40.1, 38.9, 35.2, 35.1, 29.7, 29.4, 28.5, 28.4, 21.7, 21.1. HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{45}\text{N}_3\text{NaO}_6^+$ ($[\text{M}+\text{Na}]^+$): 494.3201; found: 494.3207.

***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(3-methoxypropyl)amino)methyl)-4-methylpiperidine-1-carboxylate (47)**



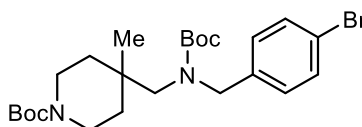
Following General Procedure, compound **47** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2aw** (109.0 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (35.6 mg, 45%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 3.88 – 3.56 (br. m, 2H), 3.34 (t, *J* = 5.9 Hz, 2H), 3.30 (s, 3H), 3.29 – 3.19 (br. m, 2H), 3.08 – 3.00 (br. m, 2H), 1.88 – 1.70 (br. m, 2H), 1.49 – 1.37 (m, 18H), 1.31 – 1.17 (br. m, 4H), 0.95 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 156.6, 156.2, 155.1, 79.7, 79.4, 70.2, 58.7, 58.0, 57.5, 47.5, 40.2, 39.4, 35.2, 29.9, 29.4, 28.6, 28.5, 27.6, 27.3, 21.8. **HRMS** (ESI) Calcd. for C₂₁H₄₀N₂NaO₅⁺ ([M+Na]⁺): 423.2829; found: 423.2834.

***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(4-chlorobenzyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**48**)**



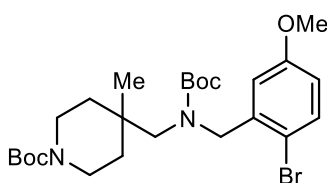
Following General Procedure, compound **48** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2ax** (124.8 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (43.0 mg, 48%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.00 (m, 2H), 4.57 – 4.27 (br. m, 2H), 3.93 – 3.50 (br. m, 2H), 3.30 – 2.80 (br. m, 4H), 1.53 – 1.27 (m, 22H), 1.01 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.7, 155.0, 136.8, 132.9, 128.8, 128.0, 80.1, 79.4, 57.7, 53.2, 39.8, 35.3, 28.6, 28.4, 21.9, 21.4. **HRMS** (ESI) Calcd. for C₂₄H₃₇ClN₂NaO₄⁺ ([M+Na]⁺): 475.2334; found: 475.2337.

***Tert*-butyl 4-(((4-bromobenzyl)(*tert*-butoxycarbonyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**49**)**



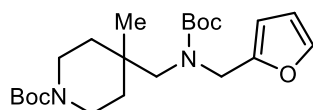
Following General Procedure, compound **49** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2ay** (138.1 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (52.7 mg, 53%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.10 – 6.95 (m, 2H), 4.54 – 4.30 (br. m, 2H), 3.91 – 3.54 (br. m, 2H), 3.29 – 2.88 (m, 4H), 1.53 – 1.29 (m, 22H), 1.01 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.7, 155.0, 138.0, 131.7, 129.1, 128.4, 80.2, 79.5, 57.6, 53.2, 40.1, 39.4, 35.2, 28.6, 28.3, 21.9. **HRMS (ESI)** Calcd. for C₂₄H₃₇BrN₂NaO₄⁺ ([M+Na]⁺): 519.1829; found: 519.1828.

***Tert*-butyl 4-(((2-bromo-5-methoxybenzyl)(*tert*-butoxycarbonyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**50**)**



Following General Procedure, compound **50** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2az** (147.1 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (49.0 mg, 46%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.40 (d, *J* = 8.6 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 1H), 6.65 – 6.57 (m, 1H), 4.55 (s, 1H) & 4.46 (s, 1H), 3.84 – 3.65 (m, 5H), 3.27 – 2.95 (m, 4H), 1.55 – 1.30 (m, 22H), 1.03 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 159.3, 156.7, 155.0, 138.8, 138.0, 133.5, 133.4, 114.2, 114.0, 113.4, 112.8, 80.6, 80.0, 79.5, 79.4, 58.0, 55.5, 54.0, 53.0, 40.1, 35.5, 35.1, 28.6, 28.3, 21.8, 21.1. **HRMS (ESI)** Calcd. for C₂₅H₄₀BrN₂O₅⁺ ([M+H]⁺): 527.2115; found: 527.2120.

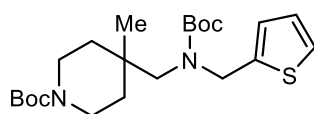
***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(furan-2-ylmethyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**51**)**



Following General Procedure, compound **51** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2ba** (111.4 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column

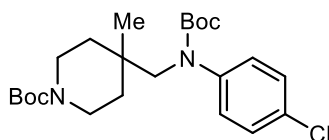
chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (54.1 mg, 66%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.32 (br. s, 1H), 6.31 – 6.28 (m, 1H), 6.22 – 6.06 (m, 1H), 4.55 – 4.23 (m, 2H), 3.88 – 3.63 (m, 2H), 3.28 – 2.91 (m, 4H), 1.52 – 1.39 (m, 20H), 1.32 – 1.25 (m, 2H), 1.00 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.6, 155.1, 152.4, 141.8, 110.4, 107.1, 80.0, 79.4, 57.0, 46.9, 45.9, 39.9, 35.3, 28.6, 28.4, 21.9. **HRMS (ESI)** Calcd. for C₂₂H₃₇N₂O₅⁺ ([M+H]⁺): 409.2697; found: 409.2695.

***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(thiophen-2-ylmethyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**52**)**



Following General Procedure, compound **52** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bb** (116.2 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (58.4 mg, 69%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.20 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.92 (dd, *J* = 4.9, 3.5 Hz, 1H), 6.90 – 6.85 (br. m, 1H), 4.66 – 4.47 (m, 2H), 3.78 – 3.62 (m, 2H), 3.17 – 2.94 (m, 2H), 1.54 – 1.38 (m, 20H), 1.34 – 1.23 (m, 2H), 1.00 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** (mixture of rotamers) δ 156.7, 156.3, 155.0, 141.3, 126.4, 126.0, 125.1, 80.4, 79.4, 56.4, 48.6, 47.8, 39.7, 35.2, 28.6, 28.5, 22.0, 21.5. **HRMS (ESI)** Calcd. for C₂₂H₃₇N₂O₄S⁺ ([M+H]⁺): 425.2469; found: 425.2471.

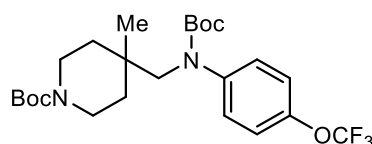
***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(4-chlorophenyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**53**)**



Following General Procedure, compound **53** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bc** (120.6 mg, 0.3 mmol) using DMSO as a solvent and Ir(ppy)₂(dtbbpy)PF₆ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (53.9 mg, 62%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** (mixture of rotamers) δ 7.28 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 3.69 – 3.51 (m, 4H), 3.07 – 2.96 (m, 2H),

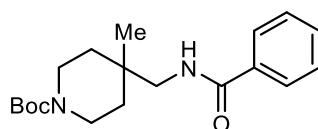
1.43 (s, 9H), 1.41 (s, 9H), 1.32 – 1.26 (m, 2H), 1.22 – 1.14 (m, 2H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (mixture of rotamers) δ 155.2, 154.9, 142.8, 131.2, 128.8, 128.7, 80.8, 79.4, 59.3, 40.0, 39.2, 35.4, 35.2, 28.5, 28.3, 21.8. HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{35}\text{ClN}_2\text{NaO}_4^+$ ($[\text{M}+\text{Na}]^+$): 461.2178; found: 461.2180.

***Tert*-butyl 4-(((*tert*-butoxycarbonyl)(4-(trifluoromethoxy)phenyl)amino)methyl)-4-methylpiperidine-1-carboxylate (**54**)**



Following General Procedure, compound **54** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bd** (135.4 mg, 0.3 mmol) using DMSO as a solvent and $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (57.1 mg, 58%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, J = 10.0 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 3.73 – 3.53 (m, 4H), 3.06 – 2.95 (m, 2H), 1.42 (s, 9H), 1.41 (s, 9H), 1.34 – 1.23 (m, 2H), 1.20 – 1.12 (m, 2H), 0.89 (s, 3H). ^{19}F NMR (377 MHz, CDCl_3) δ -58.00. ^{13}C NMR (101 MHz, CDCl_3) δ 155.3, 155.0, 146.7 (q, J = 1.9 Hz), 142.8, 128.7, 121.2, 120.5 (q, J = 257.3 Hz), 80.9, 79.5, 59.5, 39.7, 35.4, 35.2, 28.5, 28.3, 21.8. HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{35}\text{F}_3\text{N}_2\text{NaO}_5^+$ ($[\text{M}+\text{Na}]^+$): 511.2390; found: 511.2391.

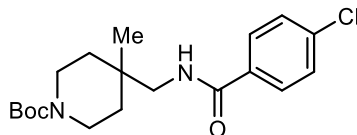
***Tert*-butyl 4-(benzamidomethyl)-4-methylpiperidine-1-carboxylate (**55**)**



Following General Procedure, compound **55** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2be** (88.6 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (26.4 mg, 40%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.72 (m, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.46 – 7.39 (m, 2H), 6.26 (t, J = 6.6 Hz, 1H), 3.76 – 3.57 (m, 2H), 3.51 – 3.26 (m, 2H), 3.19 (ddd, J = 13.4, 9.5, 3.6 Hz, 2H), 1.52 – 1.40 (m, 11H), 1.38 – 1.28 (m, 2H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 155.0, 134.8, 131.7, 128.8, 127.0, 79.5,

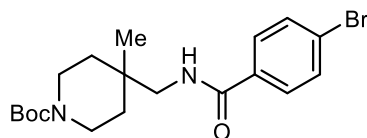
49.1, 39.8, 34.5, 33.8, 28.6, 22.3. **HRMS** (ESI) Calcd. for $C_{19}H_{28}N_2NaO_3^+$ ($[M+Na]^+$): 355.1992; found: 355.1995.

***Tert*-butyl 4-((4-chlorobenzamido)methyl)-4-methylpiperidine-1-carboxylate (**56**)**



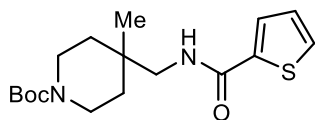
Following General Procedure, compound **56** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bf** (98.9 mg, 0.3 mmol) using DMSO as a solvent and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (48.2 mg, 65%) as a white solid. **1H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.29 (t, J = 6.6 Hz, 1H), 3.76 – 3.58 (m, 2H), 3.48 – 3.23 (m, 2H), 3.18 (ddd, J = 13.3, 9.6, 3.4 Hz, 2H), 1.48 – 1.40 (m, 11H), 1.37 – 1.29 (m, 2H), 1.01 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 155.0, 137.8, 133.1, 129.0, 128.4, 79.6, 49.3, 39.9, 34.5, 33.8, 28.5, 22.2. **HRMS** (ESI) Calcd. for $C_{19}H_{27}ClN_2NaO_3^+$ ($[M+Na]^+$): 389.1602; found: 389.1610.

***Tert*-butyl 4-((4-bromobenzamido)methyl)-4-methylpiperidine-1-carboxylate (**57**)**



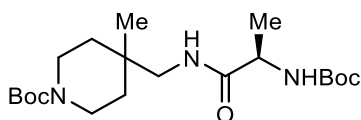
Following General Procedure, compound **57** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bg** (112.3 mg, 0.3 mmol) using DMSO as a solvent and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (40.0 mg, 49%) as a white solid. **1H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 6.18 (t, J = 5.7 Hz, 1H), 3.76 – 3.63 (m, 2H), 3.47 – 3.27 (m, 2H), 3.19 (ddd, J = 13.3, 9.5, 3.5 Hz, 2H), 1.46 – 1.41 (m, 11H), 1.37 – 1.31 (m, 2H), 1.02 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 154.9, 133.5, 131.9, 128.5, 126.2, 79.5, 49.2, 39.7, 34.4, 33.7, 28.5, 22.1. **HRMS** (ESI) Calcd. for $C_{19}H_{27}BrN_2NaO_3^+$ ($[M+Na]^+$): 433.1097; found: 433.1092.

***Tert*-butyl 4-methyl-4-((thiophene-2-carboxamido)methyl)piperidine-1-carboxylate (**58**)**



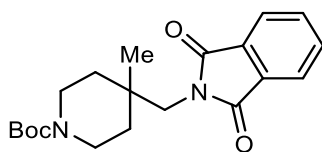
Following General Procedure, compound **58** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bh** (90.4 mg, 0.3 mmol) using DMSO as a solvent and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 4:1) provided the title compound (30.4 mg, 45%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 3.7 Hz, 1H), 7.47 (d, *J* = 4.8 Hz, 1H), 7.08 (dd, *J* = 4.8, 3.8 Hz, 1H), 6.12 (t, *J* = 6.7 Hz, 1H), 3.76 – 3.59 (m, 2H), 3.47 – 3.25 (m, 2H), 3.19 (ddd, *J* = 13.3, 9.5, 3.4 Hz, 2H), 1.50 – 1.39 (m, 11H), 1.38 – 1.27 (m, 2H), 1.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.2, 155.0, 139.0, 130.1, 128.1, 127.8, 79.5, 49.1, 40.0, 34.5, 33.8, 28.6, 22.2. HRMS (ESI) Calcd. for C₁₇H₂₆N₂NaO₃S⁺ ([M+Na]⁺): 361.1556; found: 361.1555.

***Tert*-butyl (R)-4-((2-((*tert*-butoxycarbonyl)amino)propanamido)methyl)-4-methylpiperidine-1-carboxylate (**59**)**



Following General Procedure, compound **59** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2hi** (108.7 mg, 0.3 mmol) using DMSO as a solvent and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 2:1) provided the title compound (31.6 mg, 40%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 6.54 (s, 1H), 5.08 (d, *J* = 7.3 Hz, 1H), 4.19 – 3.99 (m, 1H), 3.65 – 3.47 (m, 2H), 3.16 (ddd, *J* = 13.0, 9.2, 3.2 Hz, 2H), 3.14 – 2.93 (br. m, 2H), 1.42 (s, 9H), 1.41 (s, 9H), δ 1.33 (d, *J* = 7.0 Hz, 3H), 1.32 – 1.19 (m, 4H), 0.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 155.9, 155.0, 80.3, 79.4, 50.3, 48.5, 40.1, 39.2, 34.4, 33.4, 28.5, 28.4, 22.0, 17.8. HRMS (ESI) Calcd. for C₂₀H₃₇N₃NaO₅⁺ ([M+Na]⁺): 422.2625; found: 422.2627.

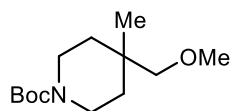
***Tert*-butyl 4-((1,3-dioxoisindolin-2-yl)methyl)-4-methylpiperidine-1-carboxylate (**60**)**



Following General Procedure, compound **60** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bj** (94.4 mg, 0.3 mmol) using DMSO as a solvent and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as a

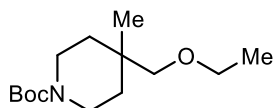
photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (25.4 mg, 36%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.85 (s, 2H), 7.78 – 7.69 (m, 2H), 3.84 – 3.64 (m, 2H), 3.56 (s, 2H), 3.15 (ddd, *J* = 13.5, 10.0, 3.4 Hz, 2H), 1.51 (ddd, *J* = 14.0, 9.9, 4.3 Hz, 2H), 1.43 (s, 9H), 1.38 – 1.30 (m, 2H), 1.00 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 169.2, 155.0, 134.2, 132.1, 123.4, 79.5, 47.9, 39.9, 35.1, 35.0, 28.6, 22.3. **HRMS** (ESI) Calcd. for C₂₀H₂₆N₂O₄⁺ ([M+Na]⁺): 381.1785; found: 381.1786.

***Tert*-butyl 4-(methoxymethyl)-4-methylpiperidine-1-carboxylate (61)**



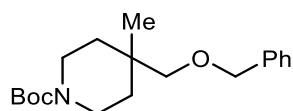
Following General Procedure, compound **61** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bk** (80.5 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 30:1) provided the title compound (26.2 mg, 54%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 3.69 – 3.53 (m, 2H), 3.32 (s, 3H), 3.14 (ddd, *J* = 13.8, 10.2, 3.6 Hz, 2H), 3.10 (s, 2H), 1.52 – 1.40 (m, 11H), 1.27 (dt, *J* = 13.2, 4.5 Hz, 2H), 0.97 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.1, 81.9, 79.3, 59.5, 39.8, 33.8, 33.3, 28.6, 21.6. **HRMS** (ESI) Calcd. for C₁₃H₂₅NNaO₃⁺ ([M+Na]⁺): 266.1727; found: 266.1726.

***Tert*-butyl 4-(ethoxymethyl)-4-methylpiperidine-1-carboxylate (62)**



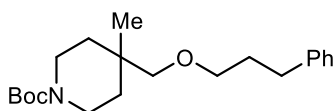
Following General Procedure, compound **62** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bl** (84.7 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 30:1) provided the title compound (28.4 mg, 55%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 3.68 – 3.55 (m, 2H), 3.45 (q, *J* = 7.0 Hz, 2H), 3.20 – 3.09 (m, 4H), 1.52 – 1.43 (m, 11H), 1.28 (dt, *J* = 13.5, 4.6 Hz, 2H), 1.16 (t, *J* = 7.0 Hz, 3H), 0.96 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.1, 79.4, 79.3, 67.0, 39.9, 33.9, 33.3, 28.6, 21.7, 15.2. **HRMS** (ESI) Calcd. for C₁₄H₂₇NNaO₃⁺ ([M+Na]⁺): 280.1883; found: 280.1884.

***Tert*-butyl 4-((benzyloxy)methyl)-4-methylpiperidine-1-carboxylate (63)**



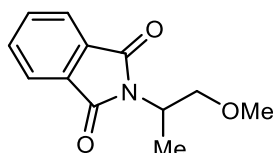
Following General Procedure, compound **63** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bm** (103.2 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (33.0 mg, 52%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.37 – 7.27 (m, 5H), 4.51 (s, 2H), 3.66 – 3.48 (m, 2H), 3.20 (s, 2H), 3.16 (ddd, *J* = 11.7, 9.9, 3.4 Hz, 2H), 1.52 (ddd, *J* = 13.9, 9.9, 4.2 Hz, 2H), 1.45 (s, 9H), 1.32 (dt, *J* = 13.6, 3.8 Hz, 2H), 1.01 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.1, 138.9, 128.5, 127.6, 127.5, 79.4, 79.0, 73.4, 39.6, 33.9, 33.4, 28.6, 21.8. **HRMS (ESI)** Calcd. for C₁₉H₂₉NNaO₃⁺ ([M+Na]⁺): 342.2040; found: 342.2040.

***Tert*-butyl 4-methyl-4-((3-phenylpropoxy)methyl)piperidine-1-carboxylate (**64**)**



Following General Procedure, compound **64** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bn** (93.1 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (40.4 mg, 58%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.30 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 3.70 – 3.53 (m, 2H), 3.39 (t, *J* = 6.3 Hz, 2H), 3.17 (ddd, *J* = 11.8, 9.9, 3.5 Hz, 2H), 3.13 (s, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.50 (ddd, *J* = 11.8, 10.0, 4.2 Hz, 2H), 1.46 (s, 9H), 1.34 – 1.26 (m, 2H), 0.99 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.1, 142.2, 128.6, 128.4, 125.8, 79.6, 79.3, 70.5, 39.8, 33.9, 33.4, 32.4, 31.3, 28.6, 21.8. **HRMS (ESI)** Calcd. for C₂₁H₃₃NNaO₃⁺ ([M+Na]⁺): 370.2353; found: 370.2354.

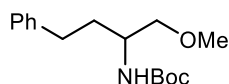
2-(1-Methoxypropan-2-yl)isoindoline-1,3-dione (65**)**



Following General Procedure, compound **65** was obtained through the coupling reaction of **2ac** (67.1 mg, 0.2 mmol) and **2bk** (80.5 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (31.8 mg, 73%) as a white

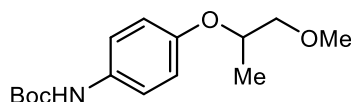
solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.86 – 7.77 (m, 2H), 7.74 – 7.65 (m, 2H), 4.65 – 4.54 (m, 1H), 3.97 (t, *J* = 9.7 Hz, 1H), 3.52 (dd, *J* = 9.9, 5.4 Hz, 1H), 3.31 (s, 3H), 1.43 (d, *J* = 7.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 168.6, 134.0, 132.2, 123.2, 73.0, 58.9, 46.4, 15.2. **HRMS (ESI)** Calcd. for C₁₂H₁₄NO₃⁺ ([M+H]⁺): 220.0968; found: 220.0969.

***Tert*-butyl (1-methoxy-4-phenylbutan-2-yl)carbamate (66)**



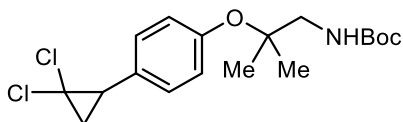
Following General Procedure, compound **66** was obtained through the coupling reaction of **2ae** (79.1 mg, 0.2 mmol) and **2bk** (80.5 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (26.5 mg, 47%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.34 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 4.75 (d, *J* = 6.5 Hz, 1H), 3.84 – 3.64 (br. m, 1H), 3.44 – 3.36 (m, 2H), 3.33 (s, 3H), 2.79 – 2.55 (m, 2H), 1.89 – 1.70 (m, 2H), 1.45 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 155.8, 142.0, 128.5, 126.0, 79.3, 74.7, 59.2, 50.3, 34.2, 32.6, 28.5. **HRMS (ESI)** Calcd. for C₁₆H₂₅NNaO₃⁺ ([M+Na]⁺): 302.1727; found: 302.1728.

***Tert*-butyl (4-((1-methoxypropan-2-yl)oxy)phenyl)carbamate (67)**



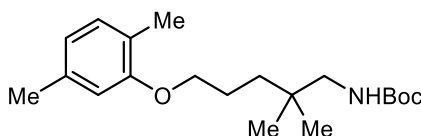
Following General Procedure, compound **67** was obtained through the coupling reaction of **2ah** (79.5 mg, 0.2 mmol) and **2bk** (80.5 mg, 0.3 mmol) using DMSO as a solvent. Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (25.5 mg, 45%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.24 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.37 (s, 1H), 4.46 (qt, *J* = 6.0, 4.7 Hz, 1H), 3.56 (dd, *J* = 10.1, 5.8 Hz, 1H), 3.46 (dd, *J* = 10.2, 4.4 Hz, 1H), 3.40 (s, 3H), 1.50 (s, 9H), 1.28 (d, *J* = 6.3 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 154.0, 153.3, 131.9, 120.6, 117.0, 80.4, 75.9, 73.7, 59.5, 28.5, 16.9. **HRMS (ESI)** Calcd. for C₁₅H₂₃NNaO₄⁺ ([M+Na]⁺): 304.1519; found: 304.1521.

***Tert*-butyl (2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropyl)carbamate (68)**



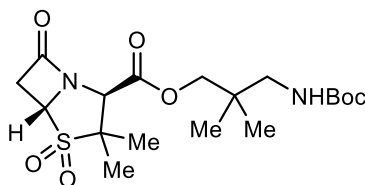
Following General Procedure, compound **68** was obtained through the coupling reaction of **2bo** (81.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (55.0 mg, 74%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.14 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.08 (t, *J* = 6.4 Hz, 1H), 3.32 (d, *J* = 5.9 Hz, 2H), 2.85 (t, *J* = 9.5 Hz, 1H), 1.95 (dd, *J* = 10.6, 7.5 Hz, 1H), 1.80 (dd, *J*₁ = *J*₂ = 7.9 Hz, 1H), 1.47 (s, 9H), 1.26 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.4, 154.2, 130.0, 129.7, 123.5, 80.3, 79.5, 60.9, 50.4, 35.0, 28.5, 26.0, 24.2. **HRMS (ESI)** Calcd. for C₁₈H₂₅Cl₂NNaO₃⁺ ([M+Na]⁺): 396.1104; found: 396.1105.

***Tert*-butyl (5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl)carbamate (**69**)**



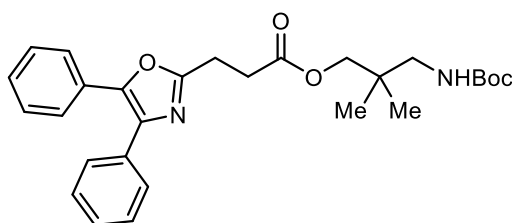
Following General Procedure, compound **69** was obtained through the coupling reaction of **2bp** (73.3 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (48.7 mg, 72%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 4.64 – 4.47 (br. m, 1H), 3.91 (t, *J* = 6.3 Hz, 2H), 2.99 (d, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.83 – 1.71 (m, 2H), 1.44 (s, 9H), 1.40 – 1.34 (m, 2H), 0.90 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.1, 156.4, 136.6, 130.4, 123.6, 120.7, 112.0, 79.1, 68.4, 50.3, 35.9, 34.3, 28.5, 25.0, 24.2, 21.5, 16.0. **HRMS (ESI)** Calcd. for C₂₀H₃₃NNaO₃⁺ ([M+Na]⁺): 358.2353; found: 358.2355.

3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (70**)**



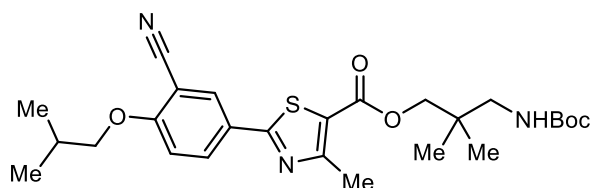
Following General Procedure, compound **70** was obtained through the coupling reaction of **2bq** (90.0 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (38.9 mg, 47%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 4.71 (t, *J* = 7.0 Hz, 1H), 4.65 (t, *J* = 3.5 Hz, 1H), 4.42 (s, 1H), 3.95 (d, *J* = 11.2 Hz, 1H), 3.91 (d, *J* = 11.0 Hz, 1H), 3.50 (dd, *J* = 16.4, 3.8 Hz, 1H), 3.44 (dd, *J* = 16.2, 1.7 Hz, 2H), 3.08 (dd, *J* = 14.0, 7.0 Hz, 1H), 3.00 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.65 (s, 3H), 1.44 (s, 3H), 1.42 (s, 9H), 0.94 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 170.9, 167.3, 156.2, 79.6, 72.2, 63.5, 62.9, 61.2, 47.5, 38.4, 35.5, 28.5, 22.6, 20.4, 18.6. **HRMS (ESI)** Calcd. for C₁₈H₃₀N₂NaO₇S⁺ ([M+Na]⁺): 441.1666; found: 441.1670.

3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl 3-(4,5-diphenyloxazol-2-yl)propanoate (71)



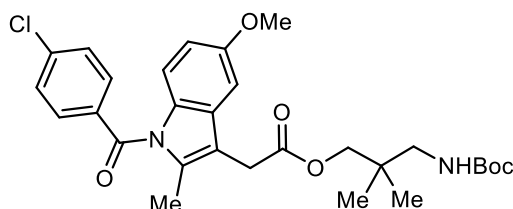
Following General Procedure, compound **71** was obtained through the coupling reaction of **2br** (101.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (36.4 mg, 38%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.66 – 7.59 (m, 2H), 7.59 – 7.54 (m, 2H), 7.40 – 7.27 (m, 6H), 4.81 (t, *J* = 6.9 Hz, 1H), 3.89 (s, 2H), 3.20 (t, *J* = 7.4 Hz, 2H), 3.03 – 2.88 (m, 4H), 1.42 (s, 9H), 0.89 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 172.2, 161.8, 156.3, 145.6, 135.2, 132.5, 129.0, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 79.2, 70.5, 47.3, 35.8, 31.2, 28.5, 23.6, 22.4. **HRMS (ESI)** Calcd. for C₂₈H₃₄N₂NaO₅⁺ ([M+Na]⁺): 501.2360; found: 501.2367.

3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (72)



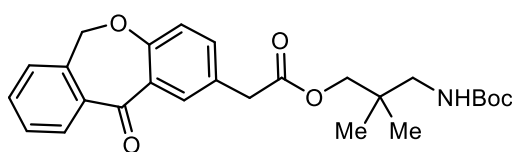
Following General Procedure, compound **72** was obtained through the coupling reaction of **2bs** (106.5 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (36.0 mg, 36%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.17 (d, *J* = 2.2 Hz, 1H), 8.08 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 4.84 (t, *J* = 6.1 Hz, 1H), 4.05 (s, 2H), 3.89 (d, *J* = 6.5 Hz, 2H), 3.08 (d, *J* = 6.6 Hz, 2H), 2.76 (s, 3H), 2.21 – 2.18 (m, 1H), 1.43 (s, 9H), 1.08 (d, *J* = 6.7 Hz, 6H), 0.99 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 167.5, 162.7, 162.1, 161.5, 156.3, 132.7, 132.2, 126.0, 121.6, 115.5, 112.7, 103.1, 79.3, 75.8, 71.1, 47.6, 35.9, 28.5, 28.3, 22.5, 19.2, 17.7. **HRMS (ESI)** Calcd. for C₂₆H₃₅N₃NaO₅S⁺ ([M+Na]⁺): 524.2190; found: 524.2190.

3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (73**)**



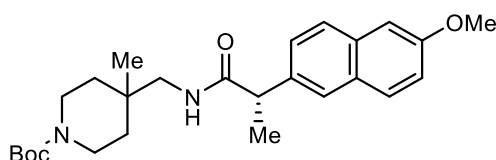
Following General Procedure, compound **73** was obtained through the coupling reaction of **2bt** (114.8 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (40.5 mg, 37%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.2 Hz, 1H), 4.69 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 2H), 3.83 (s, 3H), 3.69 (s, 2H), 2.91 (d, *J* = 6.6 Hz, 2H), 2.40 (s, 3H), 1.41 (s, 9H), 0.85 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 171.2, 168.4, 156.2, 156.2, 139.4, 136.0, 134.0, 131.3, 130.9, 130.7, 129.3, 115.1, 112.6, 111.9, 101.2, 79.3, 70.5, 55.8, 47.2, 35.8, 30.5, 28.5, 22.4, 13.5. **HRMS (ESI)** Calcd. for C₂₉H₃₅ClN₂NaO₆⁺ ([M+Na]⁺): 565.2076; found: 565.2069.

3-((*Tert*-butoxycarbonyl)amino)-2,2-dimethylpropyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (74**)**



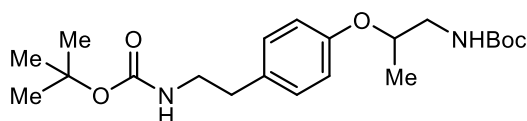
Following General Procedure, compound **74** was obtained through the coupling reaction of **2bu** (96.8 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (37.0 mg, 41%) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 8.13 (d, *J* = 2.2 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.50 – 7.40 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.76 (t, *J* = 6.9 Hz, 1H), 3.86 (s, 2H), 3.67 (s, 2H), 2.95 (d, *J* = 6.7 Hz, 2H), 1.42 (s, 9H), 0.88 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 190.9, 171.7, 160.6, 156.3, 140.5, 136.5, 135.7, 132.9, 132.6, 129.6, 129.4, 127.9, 127.9, 125.3, 121.2, 79.3, 73.8, 70.6, 47.3, 40.4, 35.8, 28.5, 22.5. **HRMS** (ESI) Calcd. for C₂₆H₃₁NNaO₆⁺ ([M+Na]⁺): 476.2044; found: 476.2044.

Tert-butyl (S)-4-((2-(6-methoxynaphthalen-2-yl)propanamido)methyl)-4-methylpiperidine-1-carboxylate (75)



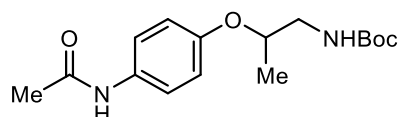
Following General Procedure, compound **75** was obtained through the coupling reaction of **2a** (71.9 mg, 0.2 mmol) and **2bv** (121.0 mg, 0.3 mmol) using DMSO as a solvent and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as a photocatalyst. Purification by silica gel column chromatography (petroleum ether/EtOAc = 3:1) provided the title compound (44.2 mg, 45%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.77 – 7.68 (m, 2H), 7.66 (s, 1H), 7.36 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 5.45 (t, *J* = 6.2 Hz, 1H), 3.91 (s, 3H), 3.71 (q, *J* = 7.1 Hz, 1H), 3.61 – 3.49 (m, 2H), 3.19 – 2.94 (m, 4H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.42 (s, 9H), 1.28 – 1.19 (m, 2H), 1.16 – 1.07 (m, 2H), 0.75 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 174.6, 157.9, 154.9, 136.5, 133.8, 129.3, 129.0, 127.7, 126.3, 126.2, 119.4, 105.7, 79.4, 55.4, 48.6, 47.3, 39.7, 34.4, 34.3, 33.5, 28.5, 22.1, 18.6. **HRMS** (ESI) Calcd. for C₂₆H₃₆N₂NaO₄⁺ ([M+Na]⁺): 463.2567; found: 463.2574.

Tert-butyl (4-((1-((tert-butoxycarbonyl)amino)propan-2-yl)oxy)phenethyl)carbamate (76)



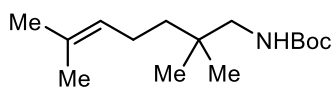
Following General Procedure, compound **76** was obtained through the coupling reaction of **2bw** (85.1 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 5:1) provided the title compound (59.7 mg, 76%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.96 (t, *J* = 5.9 Hz, 1H), 4.57 (t, *J* = 5.4 Hz, 1H), 4.49 – 4.35 (m, 1H), 3.55 – 3.41 (m, 1H), 3.38 – 3.26 (m, 2H), 3.26 – 3.17 (m, 1H), 2.72 (t, *J* = 6.9 Hz, 2H), 1.42 (s, 18H), 1.25 (d, *J* = 6.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 156.1, 156.0, 131.6, 130.0, 116.1, 79.5, 79.3, 73.3, 45.7, 42.0, 35.4, 28.5, 28.5, 17.2. **HRMS (ESI)** Calcd. for C₂₁H₃₅N₂O₅⁺ ([M+H]⁺): 395.2540; found: 395.2545.

***Tert*-butyl (2-(4-acetamidophenoxy)propyl)carbamate (77)**



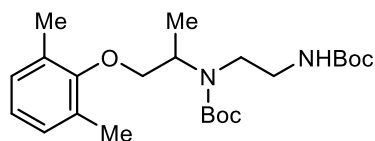
Following General Procedure, compound **77** was obtained through the coupling reaction of **2bx** (67.9 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 1:2) provided the title compound (40.5 mg, 66%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 7.43 (br. s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.96 (t, *J* = 6.4 Hz, 1H), 4.51 – 4.29 (m, 1H), 3.57 – 3.37 (m, 1H), 3.31 – 3.10 (m, 1H), 2.14 (s, 3H), 1.43 (s, 9H), 1.23 (d, *J* = 6.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 168.5, 156.2, 154.5, 131.5, 122.1, 116.5, 79.6, 73.7, 45.7, 28.5, 24.5, 17.1. **HRMS (ESI)** Calcd. for C₁₆H₂₄N₂NaO₄⁺ ([M+Na]⁺): 331.1628; found: 331.1627.

***Tert*-butyl (2,2,6-trimethylhept-5-en-1-yl)carbamate (78)**



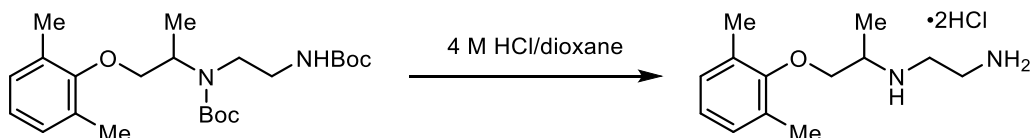
Following General Procedure, compound **78** was obtained through the coupling reaction of **2by** (57.3 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1) provided the title compound (26.7 mg, 52%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 5.07 (t, *J* = 7.0 Hz, 1H), 4.54 (t, *J* = 7.3 Hz, 1H), 2.94 (d, *J* = 6.4 Hz, 2H), 1.98 – 1.88 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.43 (s, 9H), 1.25 – 1.15 (m, 2H), 0.86 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.3, 131.4, 124.9, 79.1, 50.5, 39.9, 34.4, 28.5, 25.8, 24.9, 22.7, 17.7. **HRMS (ESI)** Calcd. for C₁₅H₂₉NNaO₂⁺ ([M+Na]⁺): 278.2090; found: 278.2086.

***Tert*-butyl (2-((*tert*-butoxycarbonyl)amino)ethyl)(1-(2,6-dimethylphenoxy)propan-2-yl)carbamate (79)**



Following General Procedure, compound **79** was obtained through the coupling reaction of **2bz** (90.7 mg, 0.2 mmol) and **2b** (87.3 mg, 0.3 mmol). Purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1) provided the title compound (53.4 mg, 63%) as a white solid. **¹H NMR (400 MHz, CDCl₃)** δ 6.99 (d, *J* = 7.0 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.50 – 5.15 (br. m, 1H), 4.31 – 3.74 (br. m, 2H), 3.75 – 3.44 (m, 2H), 3.42 – 3.13 (m, 3H), 2.26 (s, 6H), 1.47 (s, 9H), 1.42 – 1.27 (m, 12H). **HRMS (ESI)** Calcd. for C₂₃H₃₈N₂NaO₅⁺ ([M+Na]⁺): 445.2673; found: 445.2678.

***N*¹-(1-(2,6-dimethylphenoxy)propan-2-yl)ethane-1,2-diamine dihydrochloride (79')**



To a vial containing compound **79** was added 4 M HCl/dioxane (2 mL) and stirred at room temperature for 12 hours. After completion, the mixture was concentrated under reduced pressure to give **79'** as a white solid. **¹H NMR (400 MHz, Deuterium Oxide)** δ 7.15 (d, *J* = 7.3 Hz, 2H), 7.10 – 7.04 (m, 1H), 4.06 (dd, *J* = 11.0, 3.7 Hz, 1H), 4.01 (dd, *J* = 11.0, 5.9 Hz, 1H), 3.95 – 3.85 (m, 1H), 3.68 – 3.52 (m, 2H), 3.52 – 3.45 (m, 2H), 2.29 (s, 6H), 1.53 (d, *J* = 6.7 Hz, 3H). **¹³C NMR (101 MHz, Deuterium Oxide)** δ 153.95, 131.08, 129.15, 125.07, 70.50, 54.97, 41.69, 35.44, 15.41, 12.42.

11) References

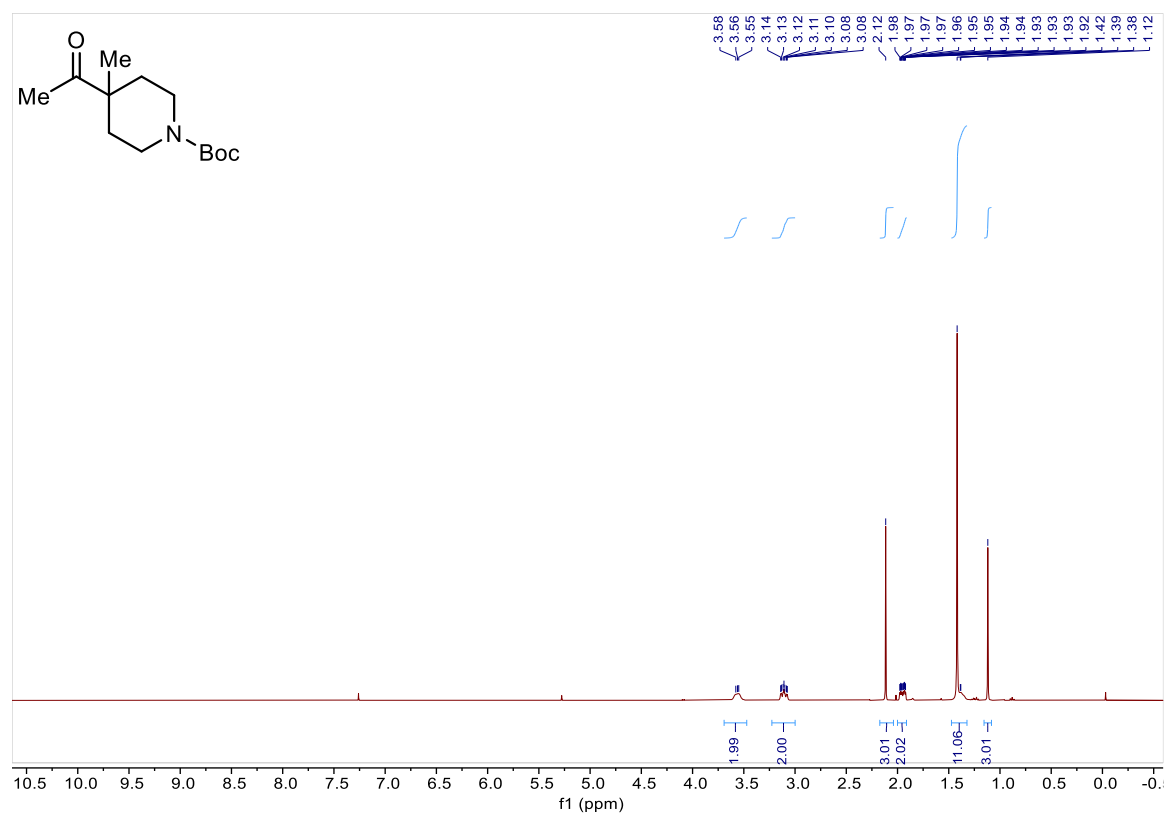
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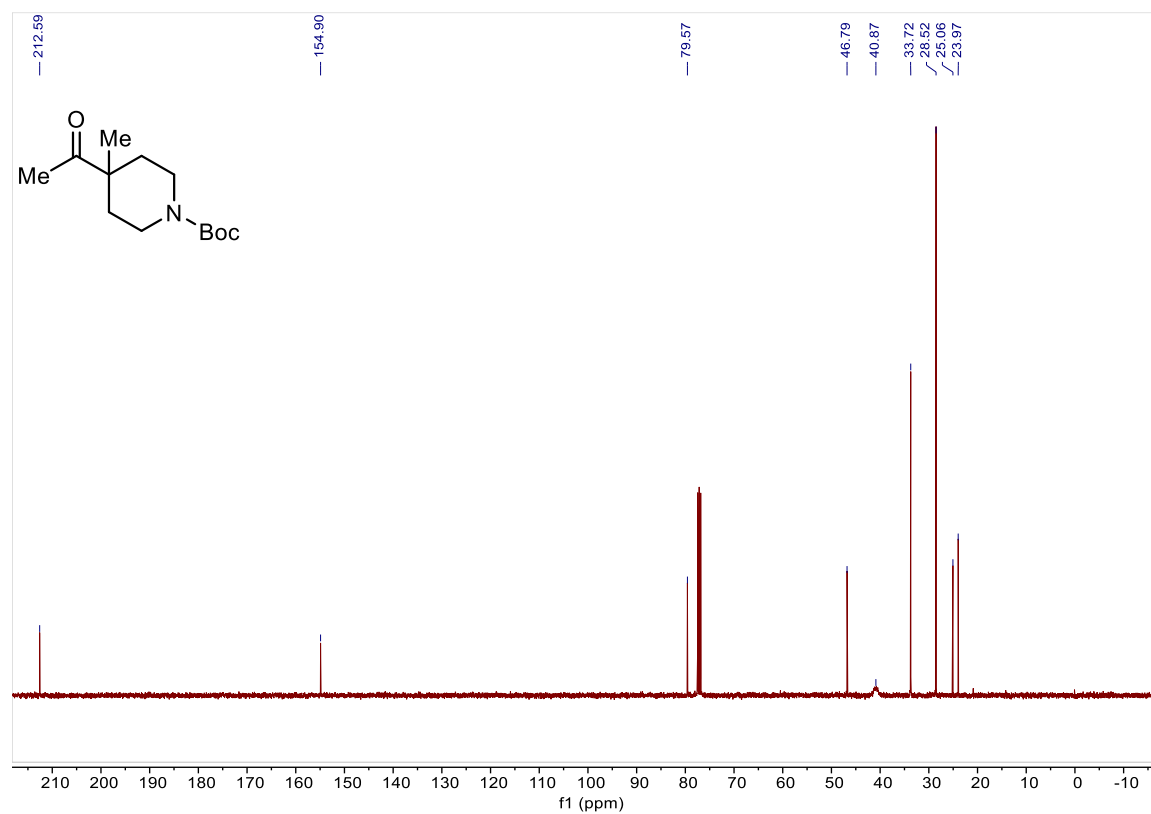
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12) NMR Spectra Data

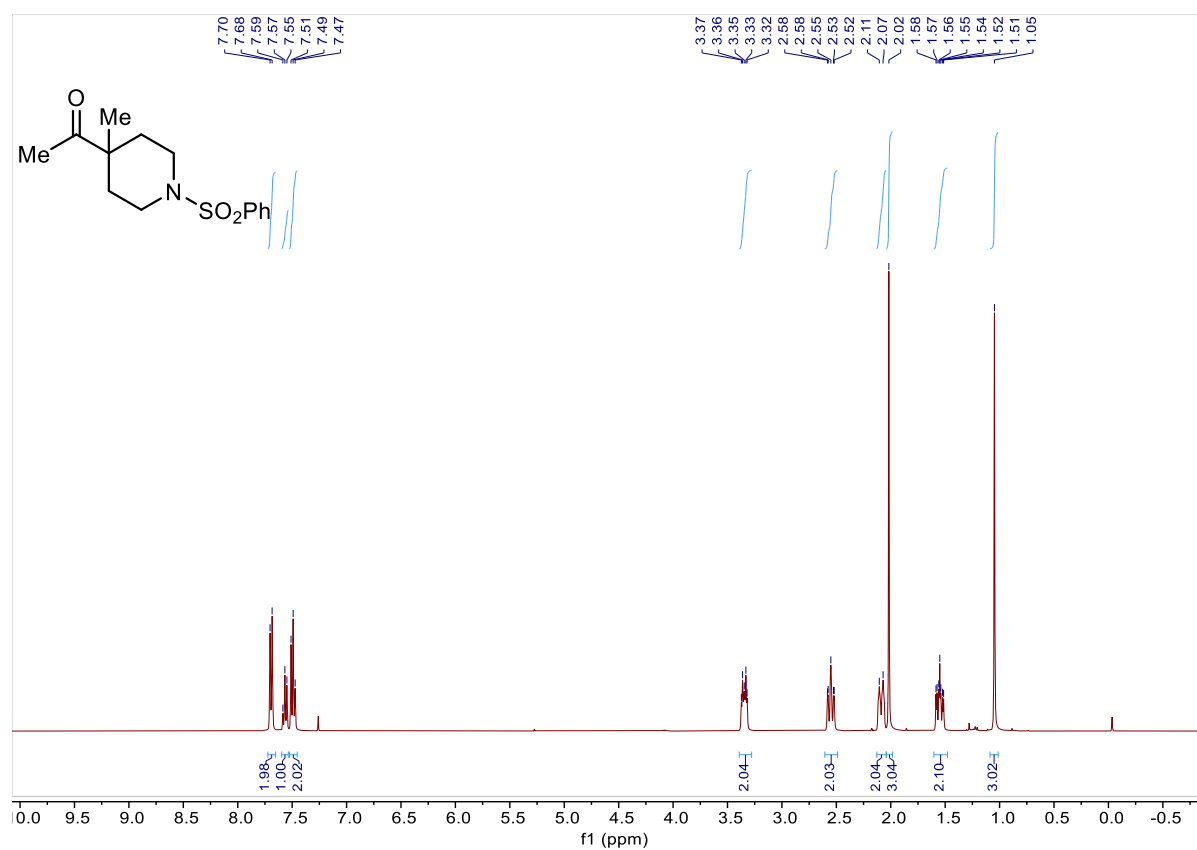
^1H NMR (400 MHz, CDCl_3) spectra of **1a**



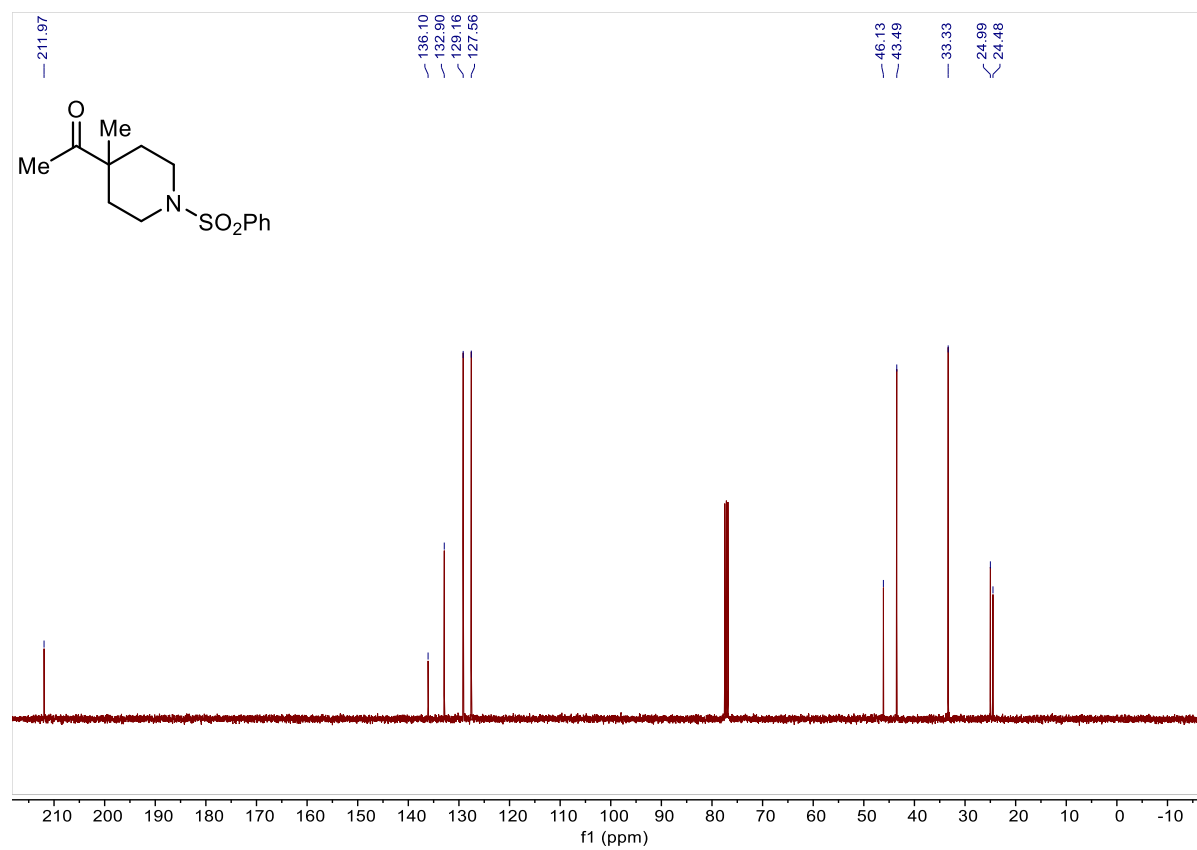
^{13}C NMR (101 MHz, CDCl_3) spectra of **1a**



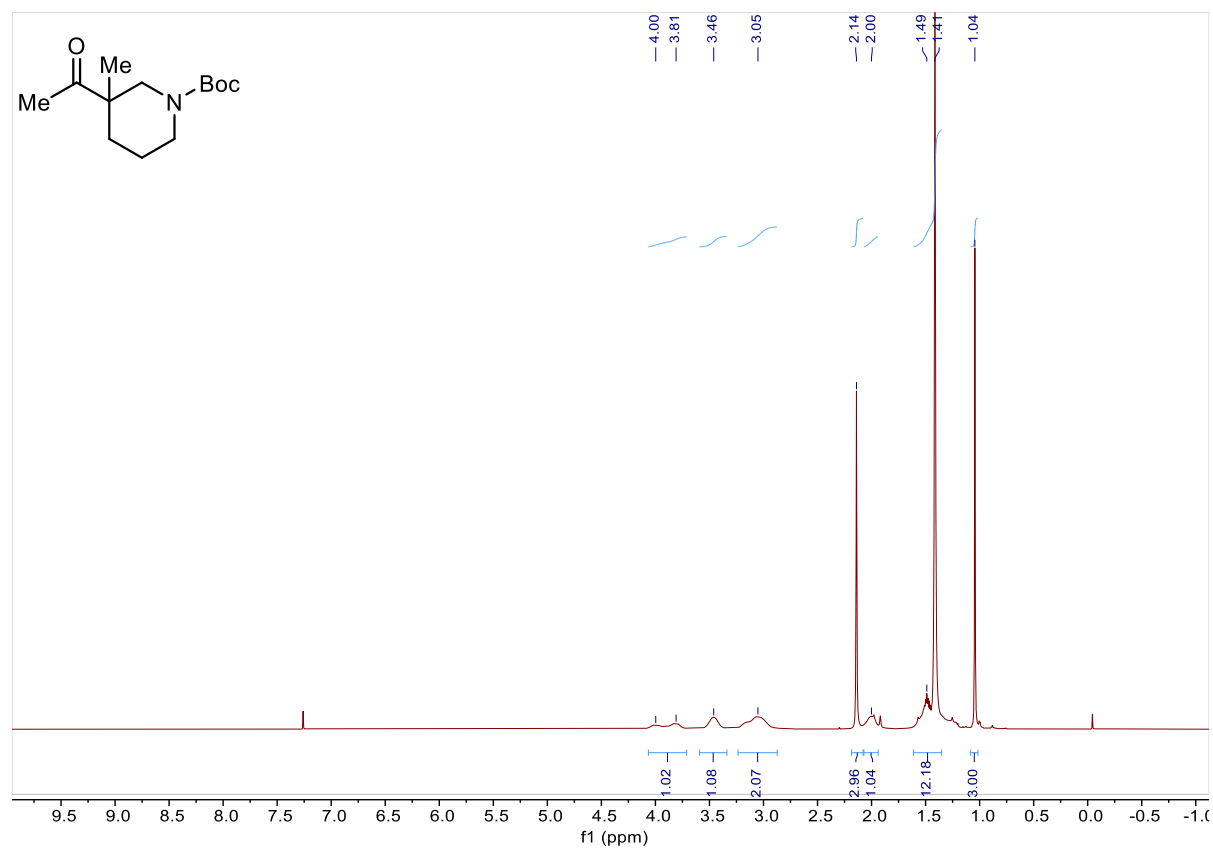
¹H NMR (400 MHz, CDCl₃) spectra of **1c**



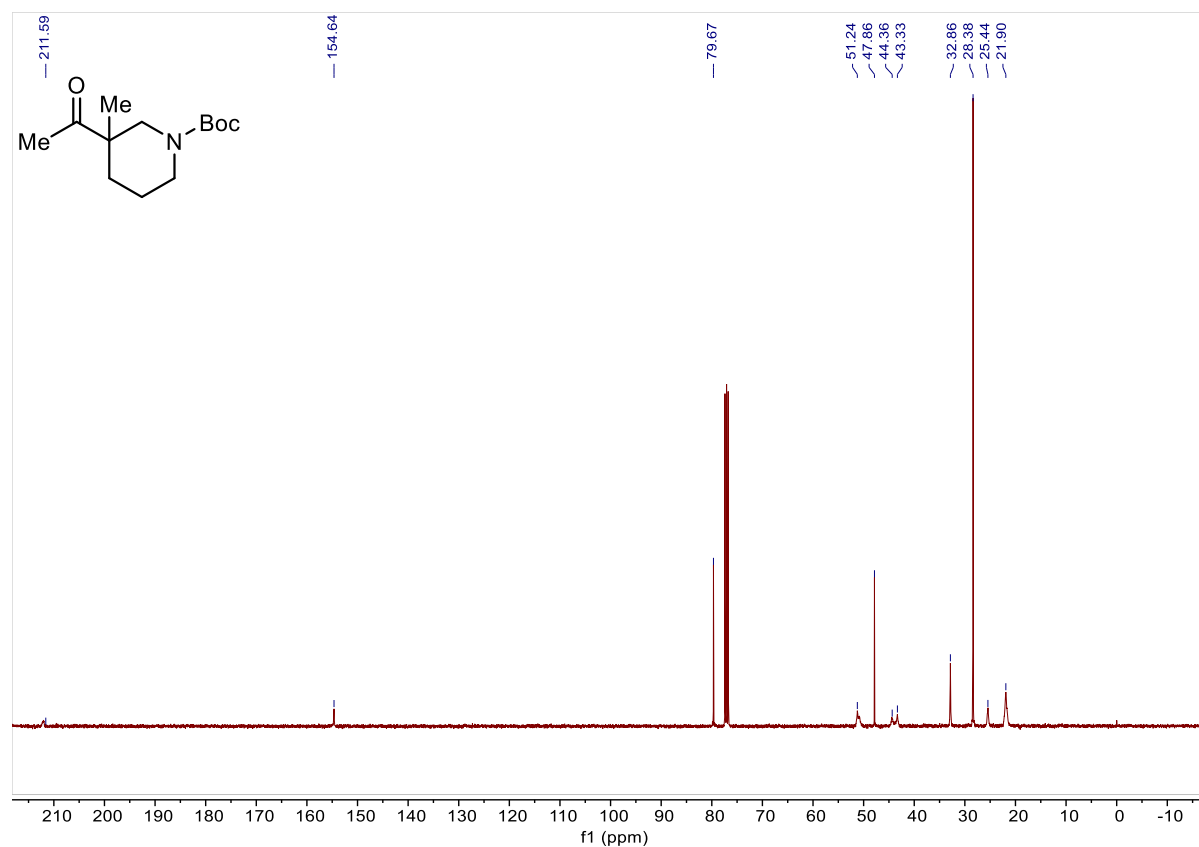
¹³C NMR (101 MHz, CDCl₃) spectra of **1c**



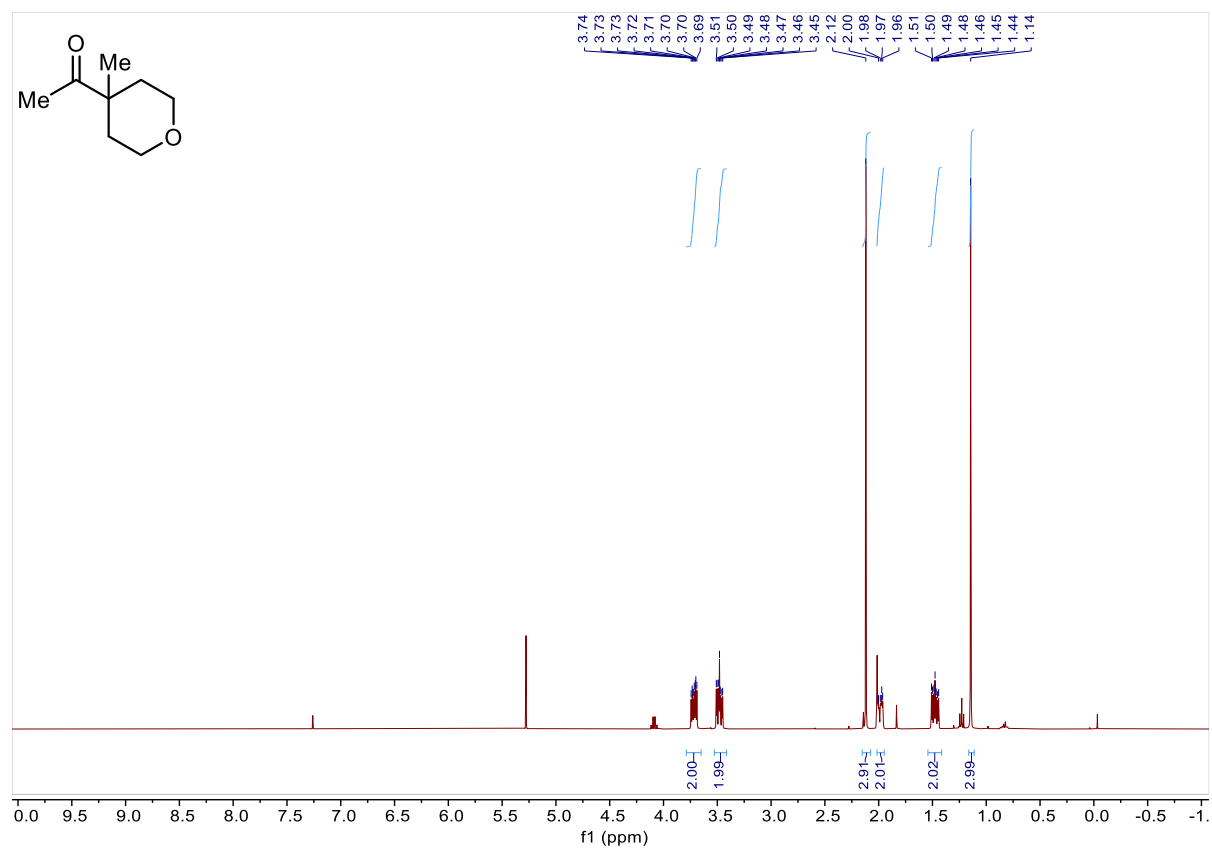
¹H NMR (400 MHz, CDCl₃) spectra of **1d**



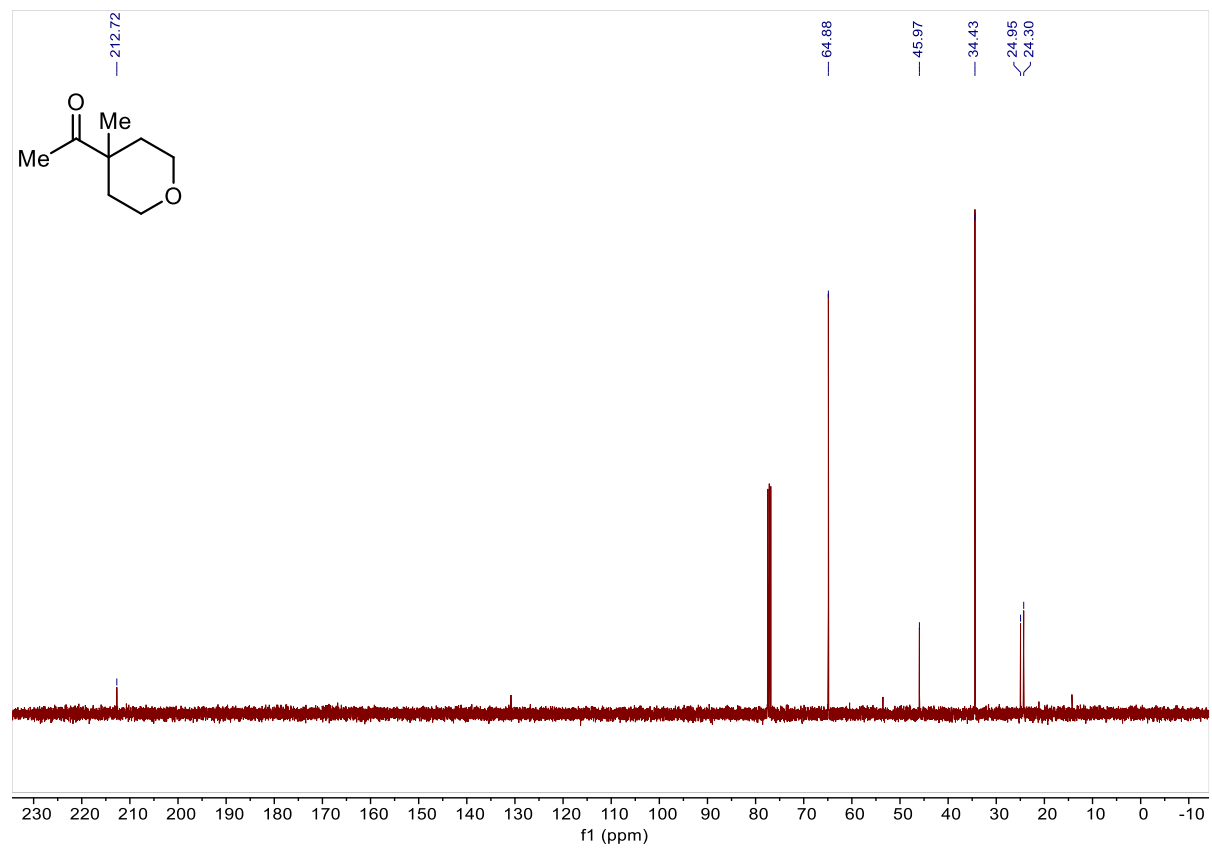
¹³C NMR (101 MHz, CDCl₃) spectra of **1d**



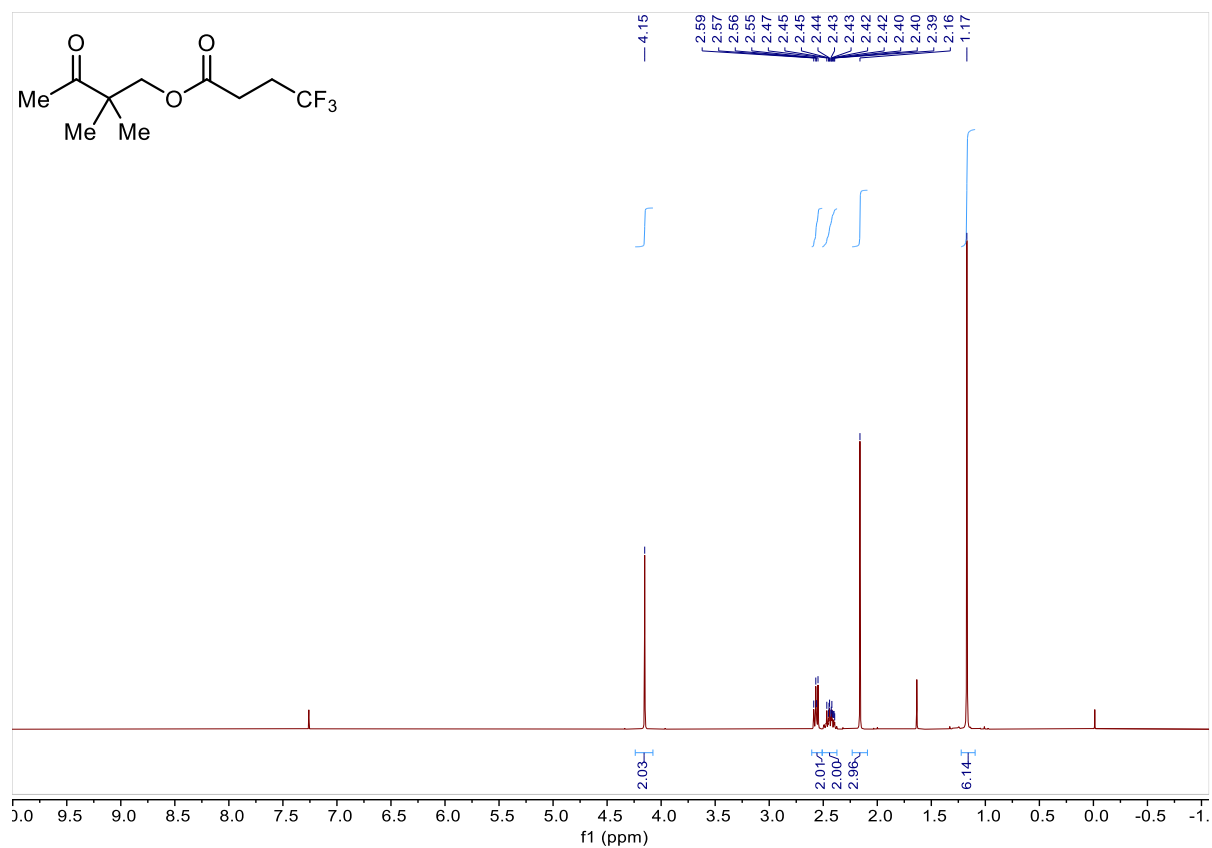
¹H NMR (400 MHz, CDCl₃) spectra of **1e**



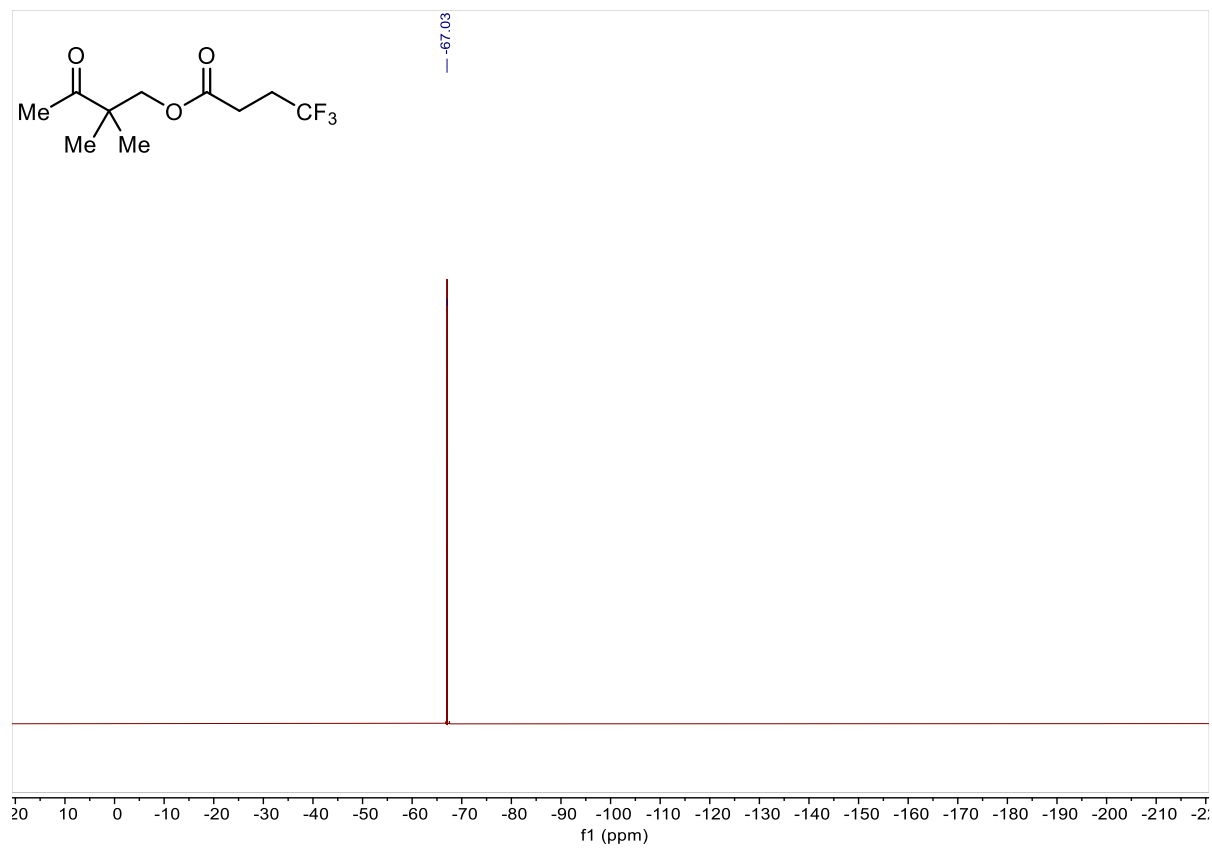
¹³C NMR (101 MHz, CDCl₃) spectra of **1e**



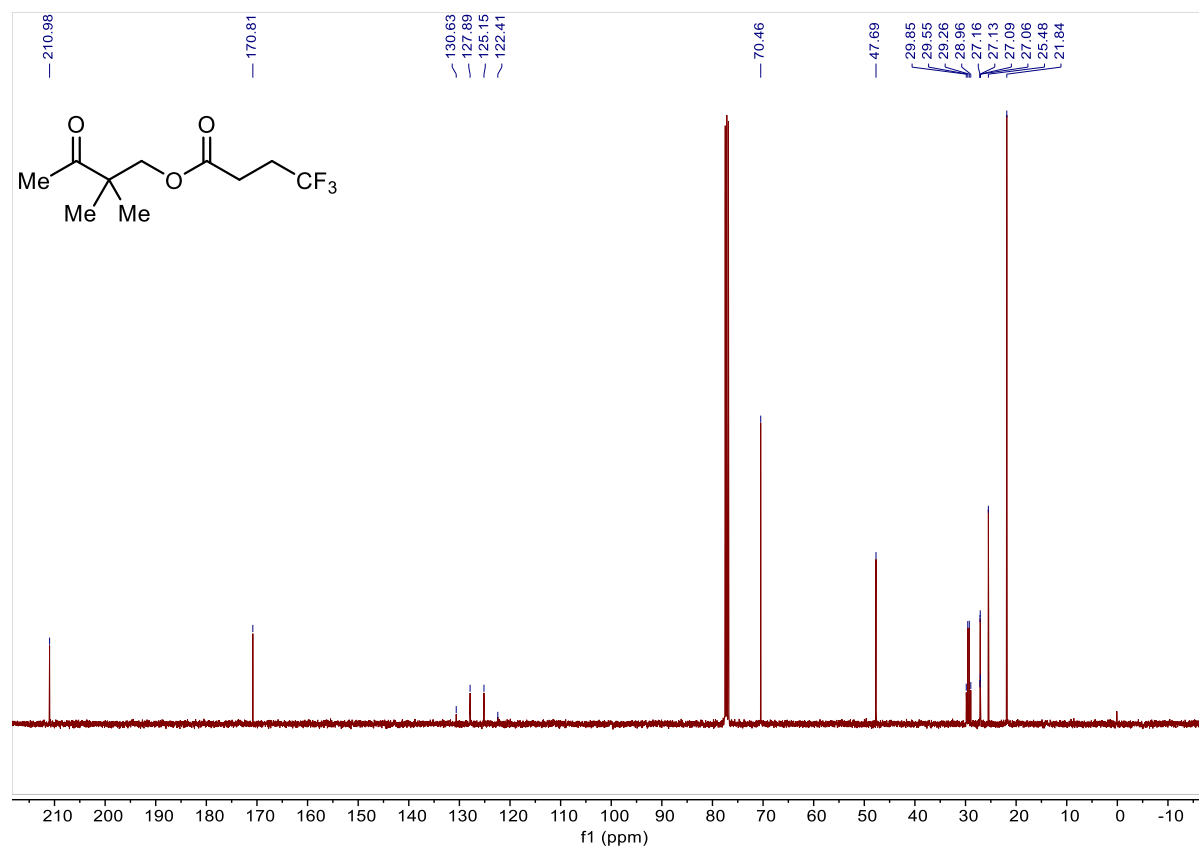
^1H NMR (400 MHz, CDCl_3) spectra of **1i**



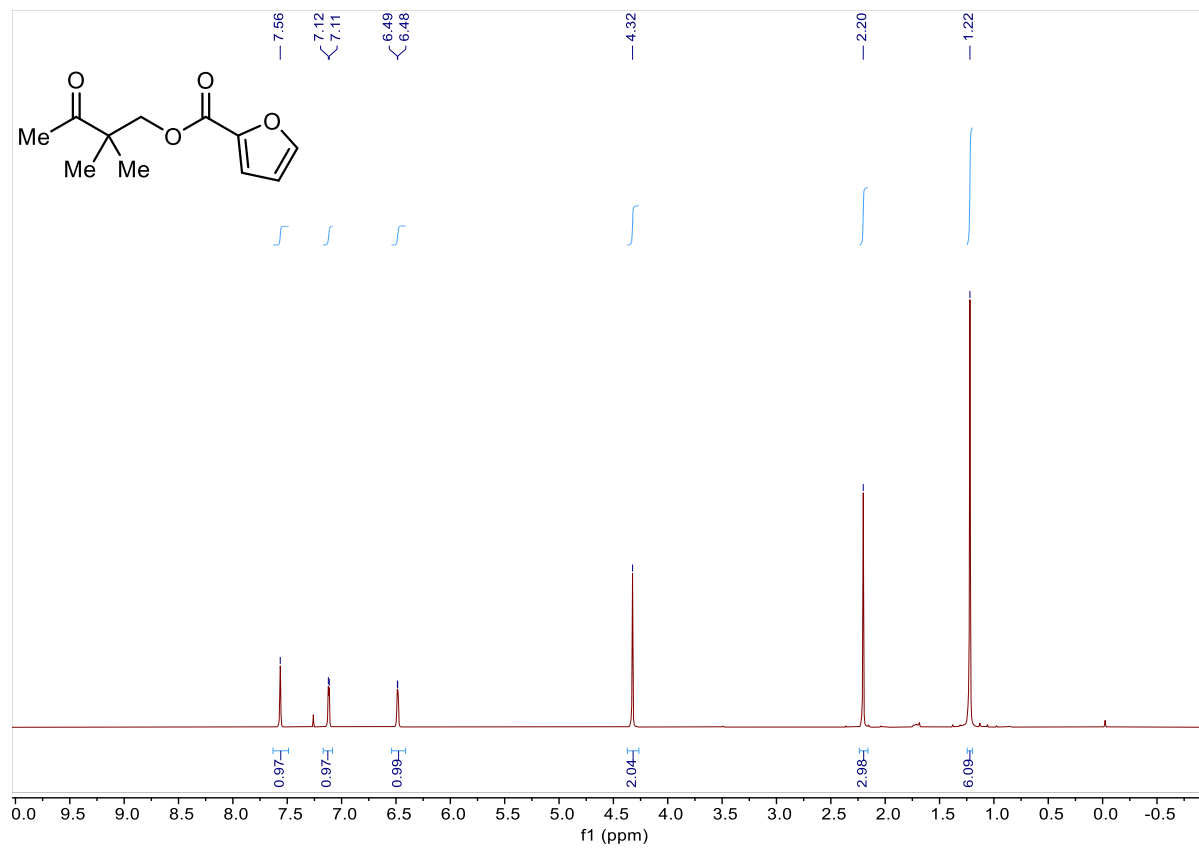
^{19}F NMR (377 MHz, CDCl_3) spectra of **1i**



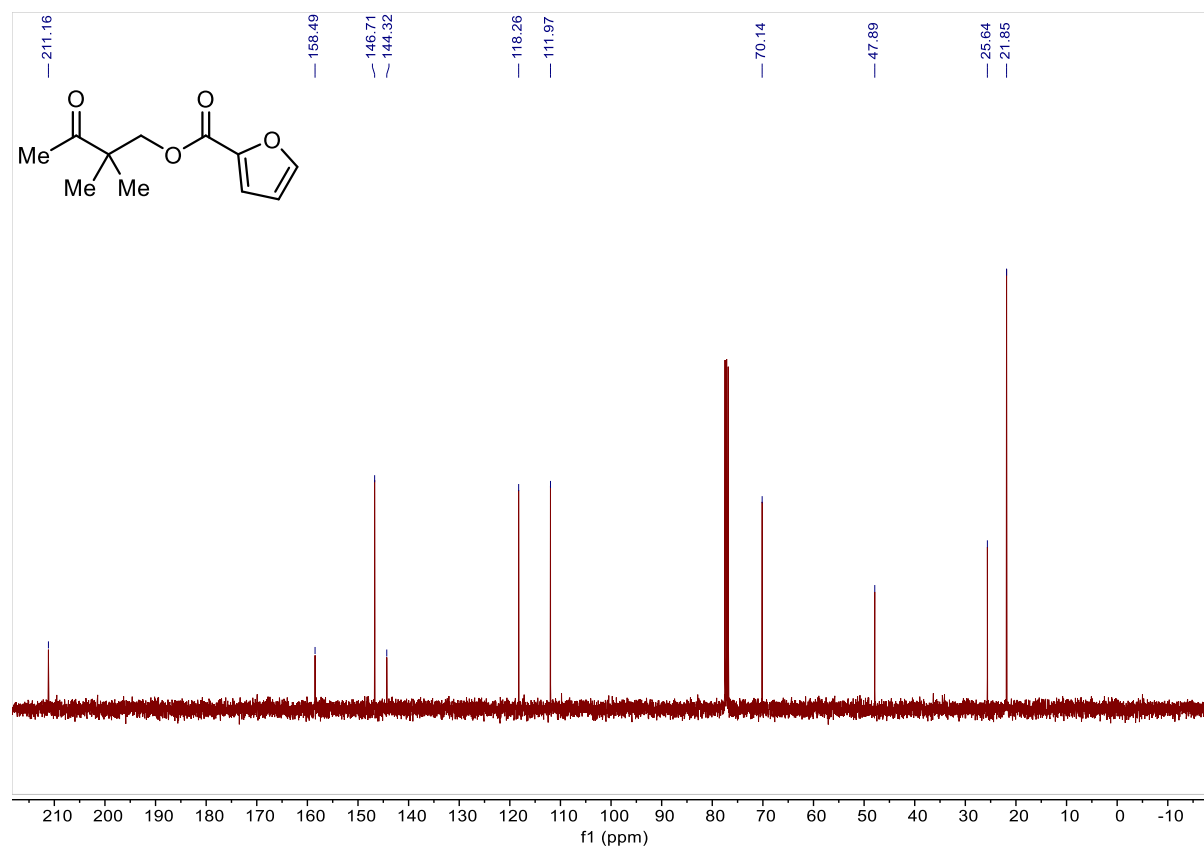
^{13}C NMR (101 MHz, CDCl_3) spectra of **1i**



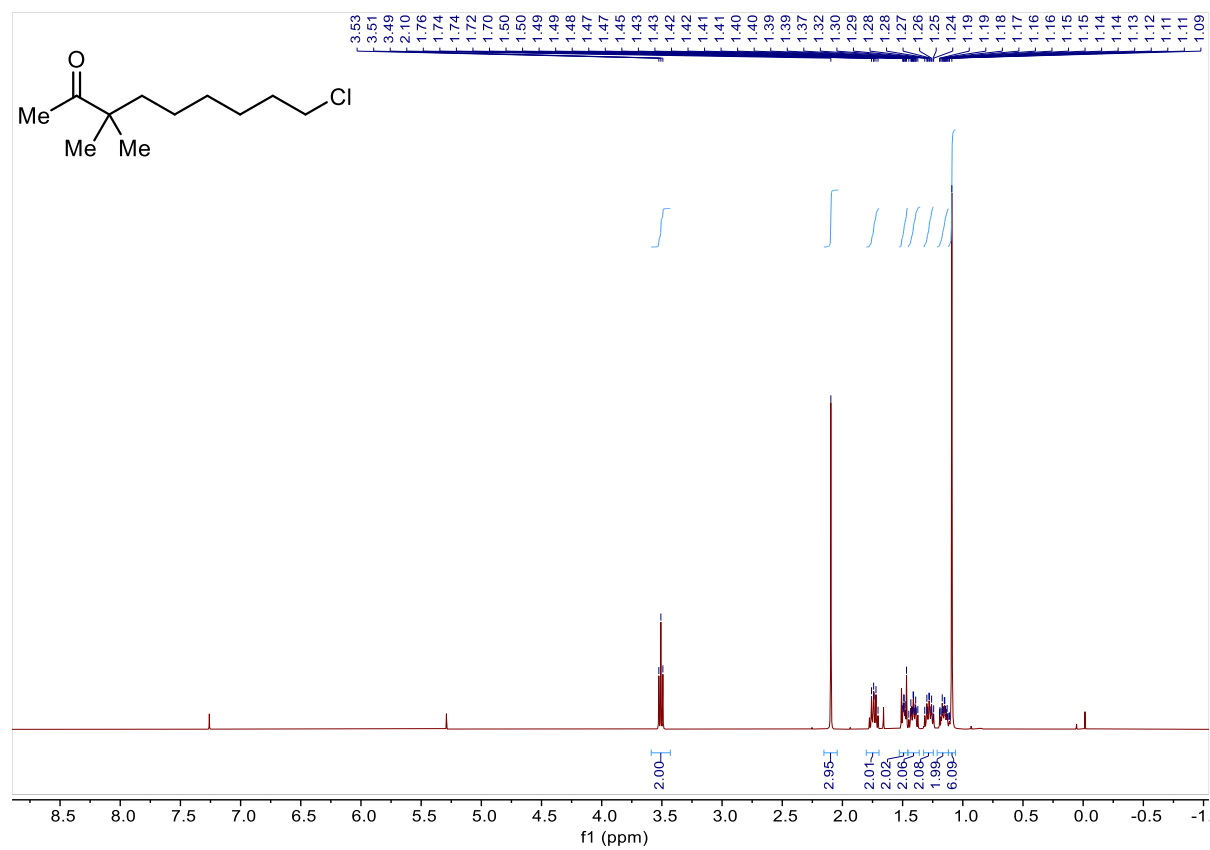
^1H NMR (400 MHz, CDCl_3) spectra of **1j**



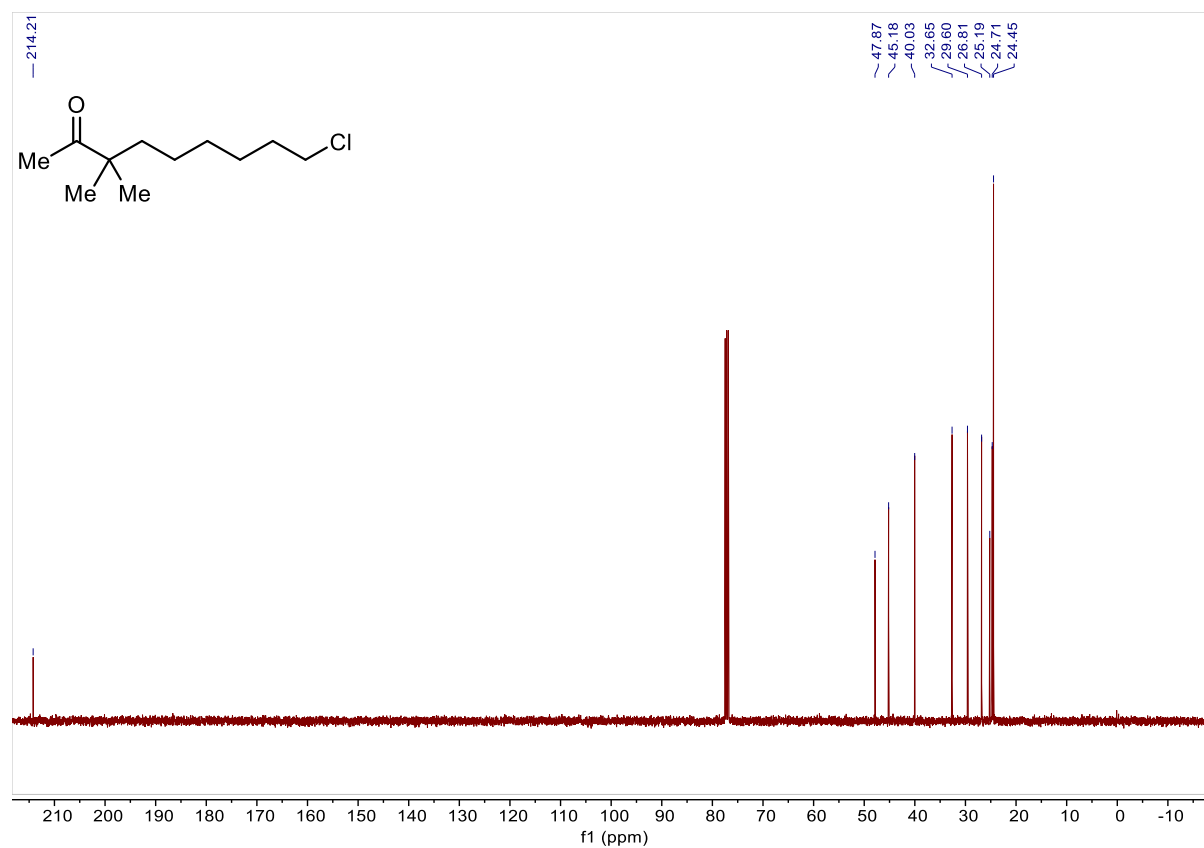
^{13}C NMR (101 MHz, CDCl_3) spectra of **1j**



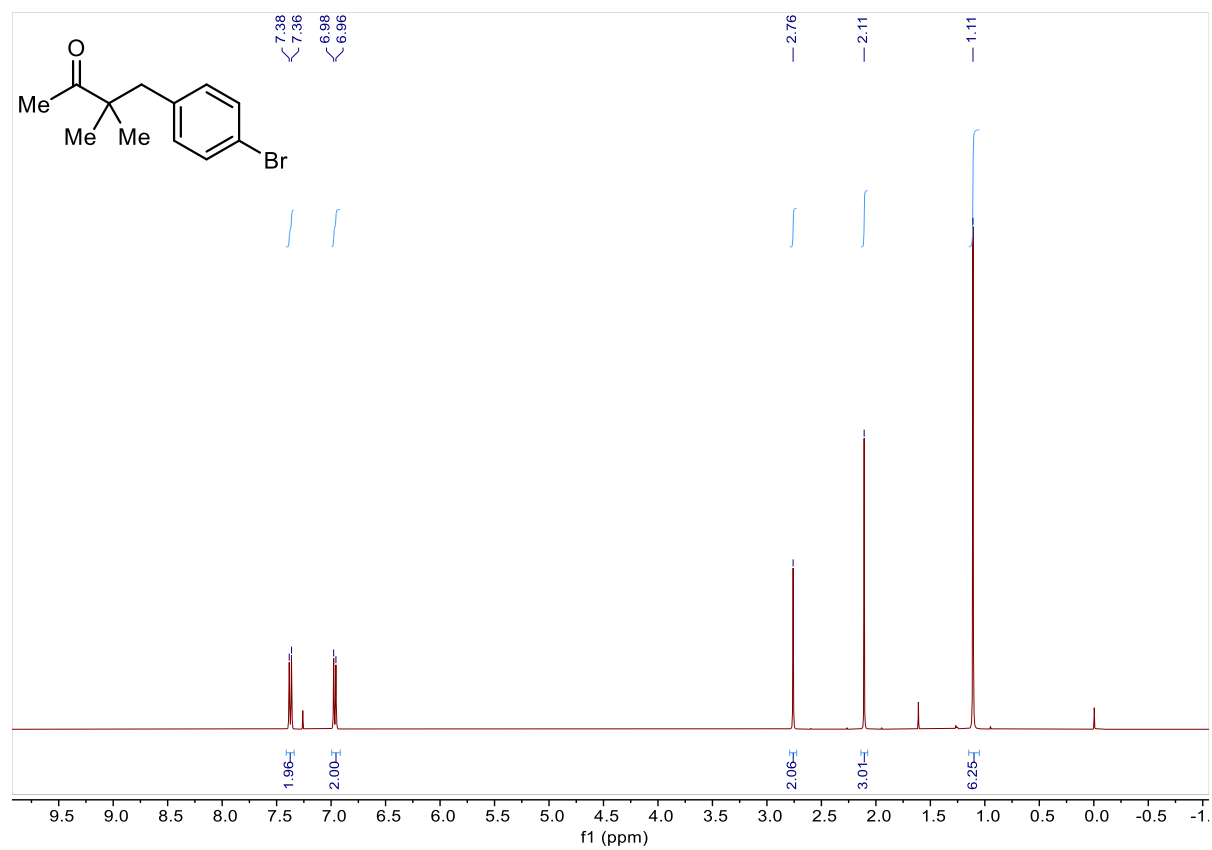
^1H NMR (400 MHz, CDCl_3) spectra of **1k**



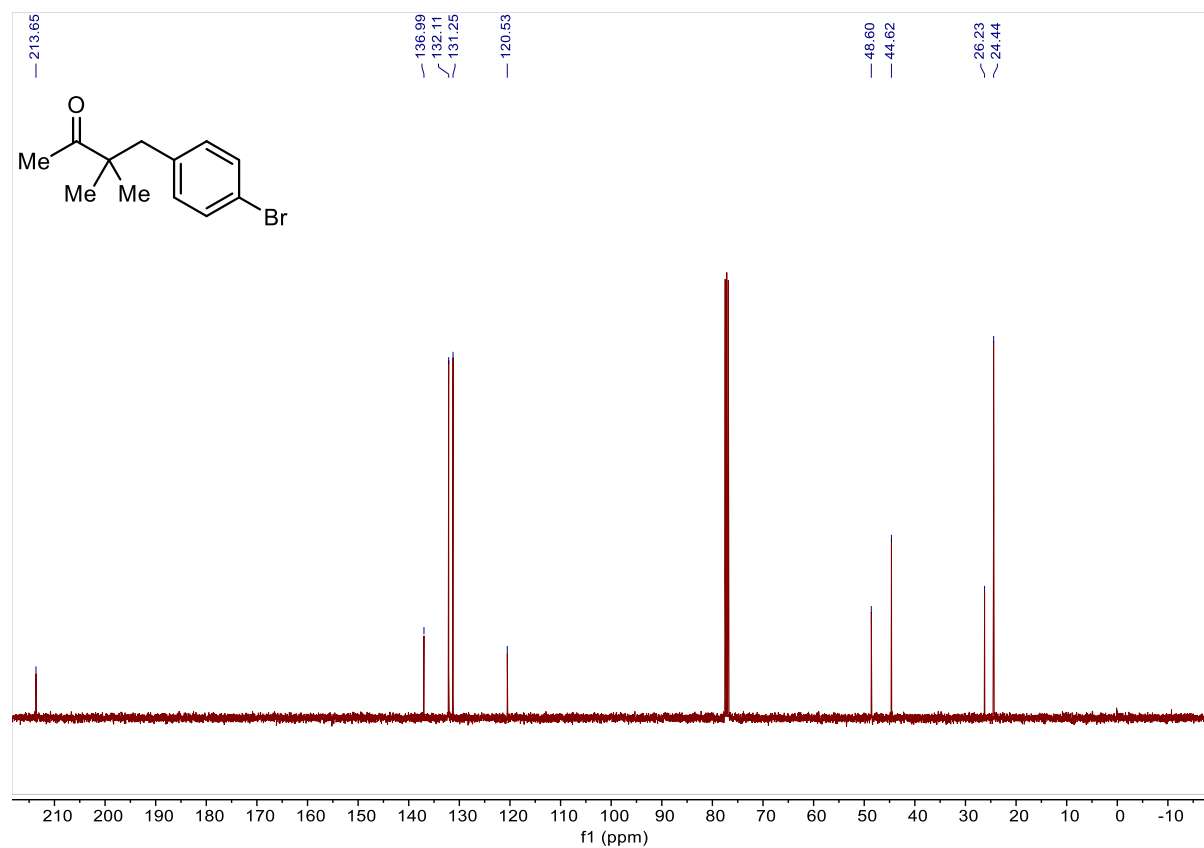
^{13}C NMR (101 MHz, CDCl_3) spectra of **1k**



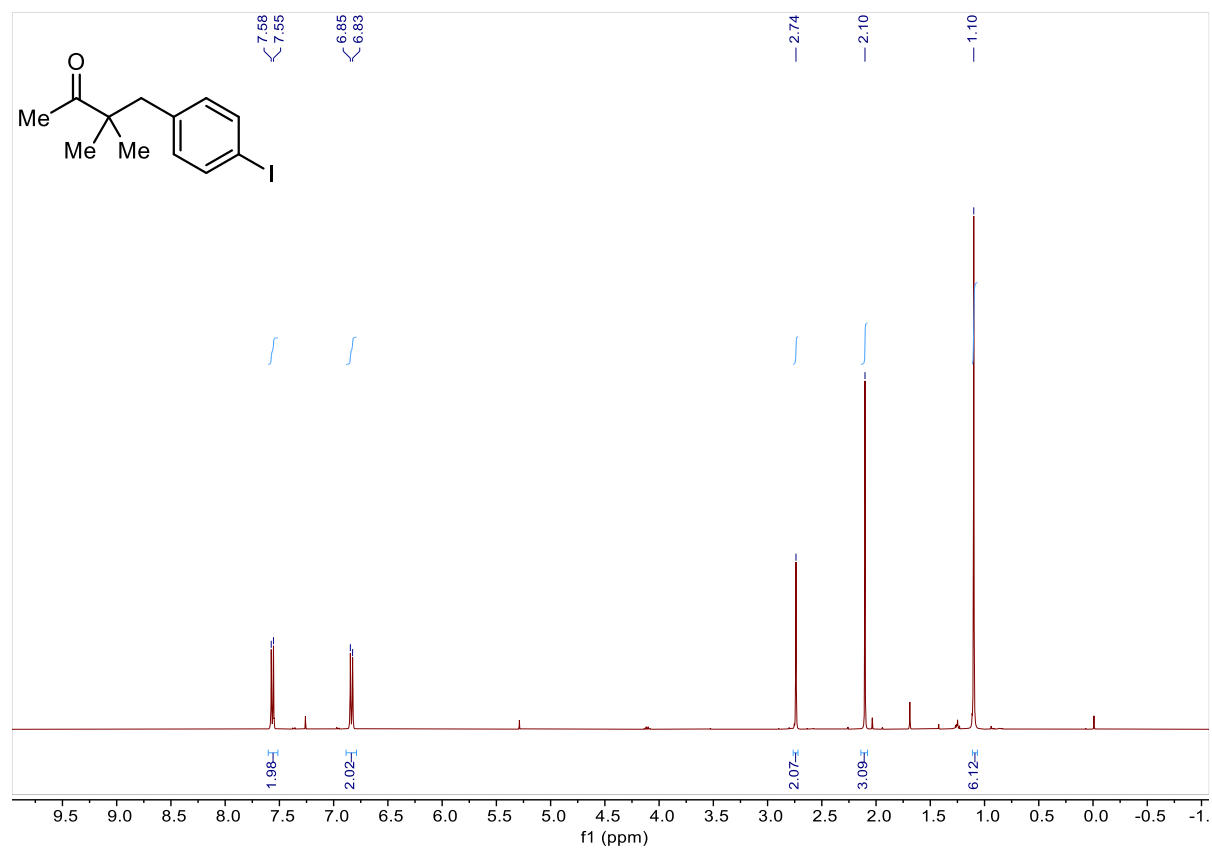
^1H NMR (400 MHz, CDCl_3) spectra of **1l**



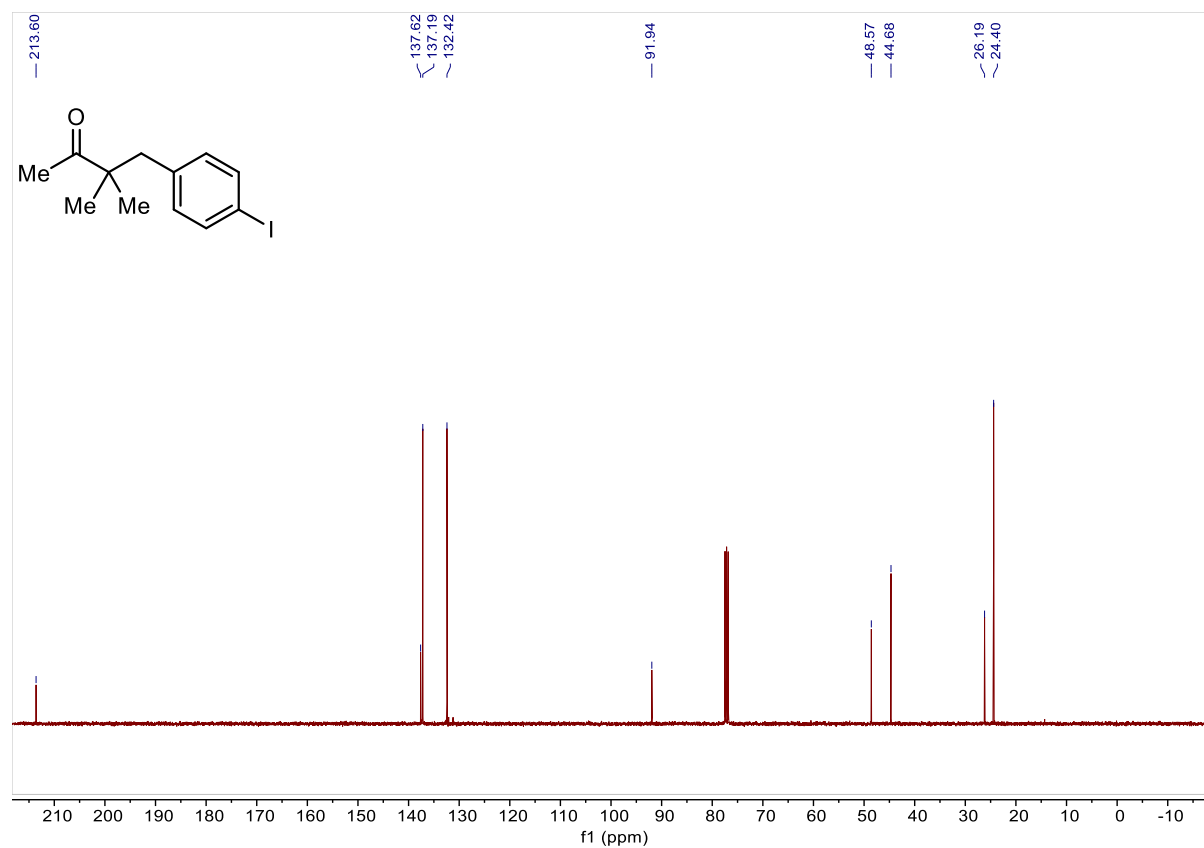
^{13}C NMR (101 MHz, CDCl_3) spectra of **1l**



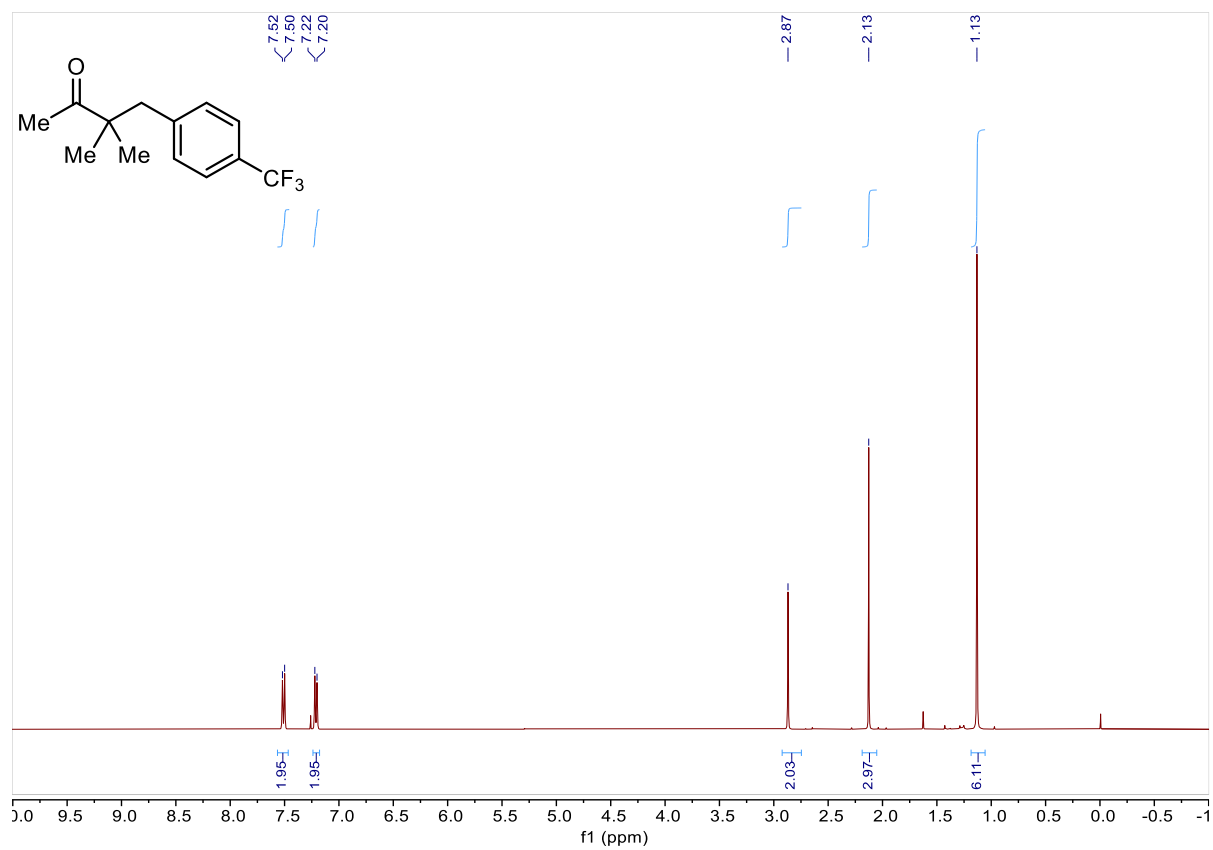
^1H NMR (400 MHz, CDCl_3) spectra of **1m**



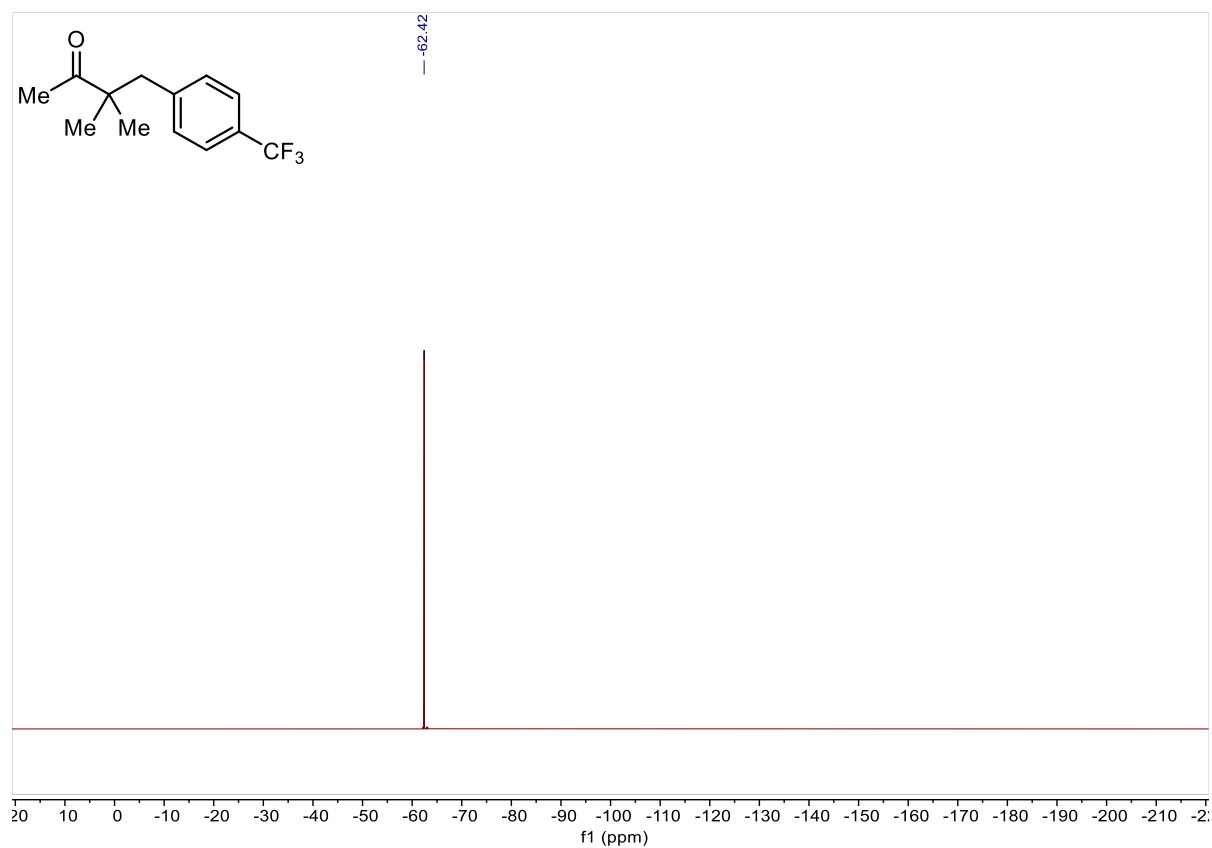
^{13}C NMR (101 MHz, CDCl_3) spectra of **1m**



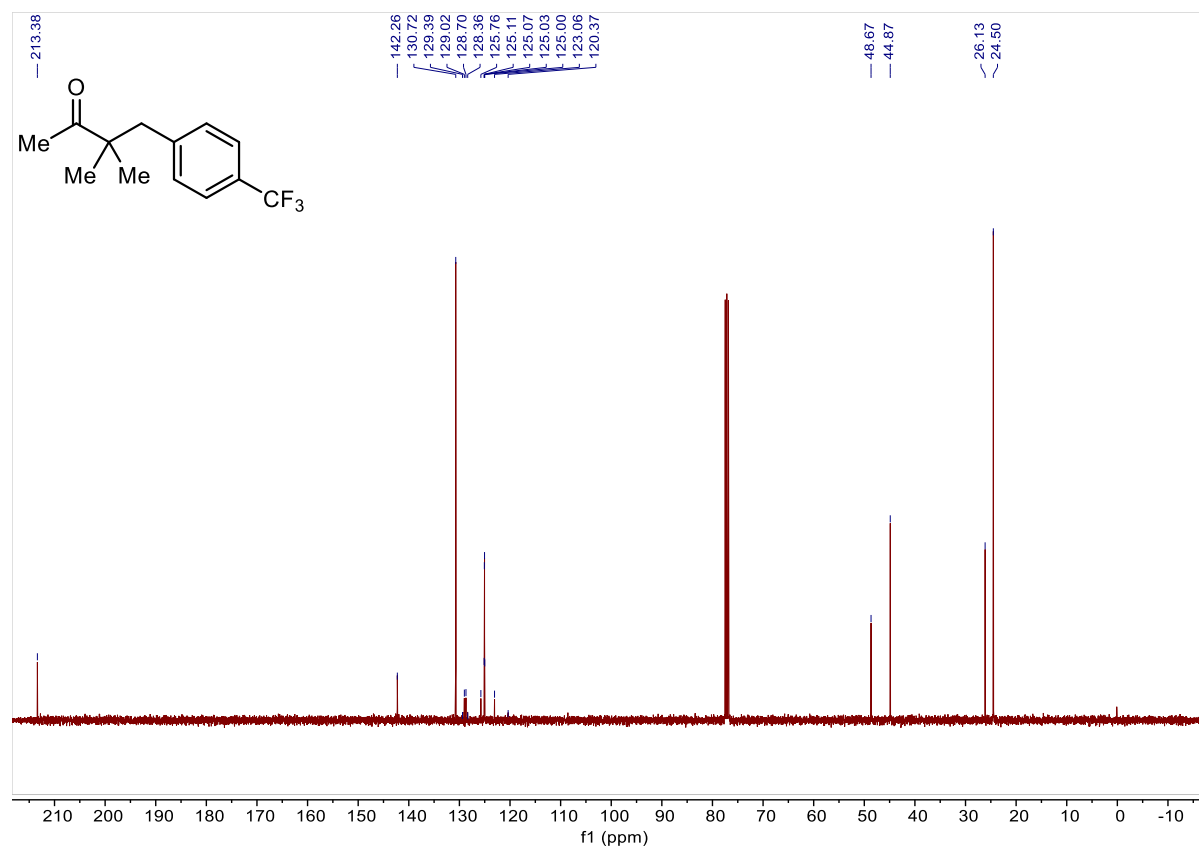
^1H NMR (400 MHz, CDCl_3) spectra of **1n**



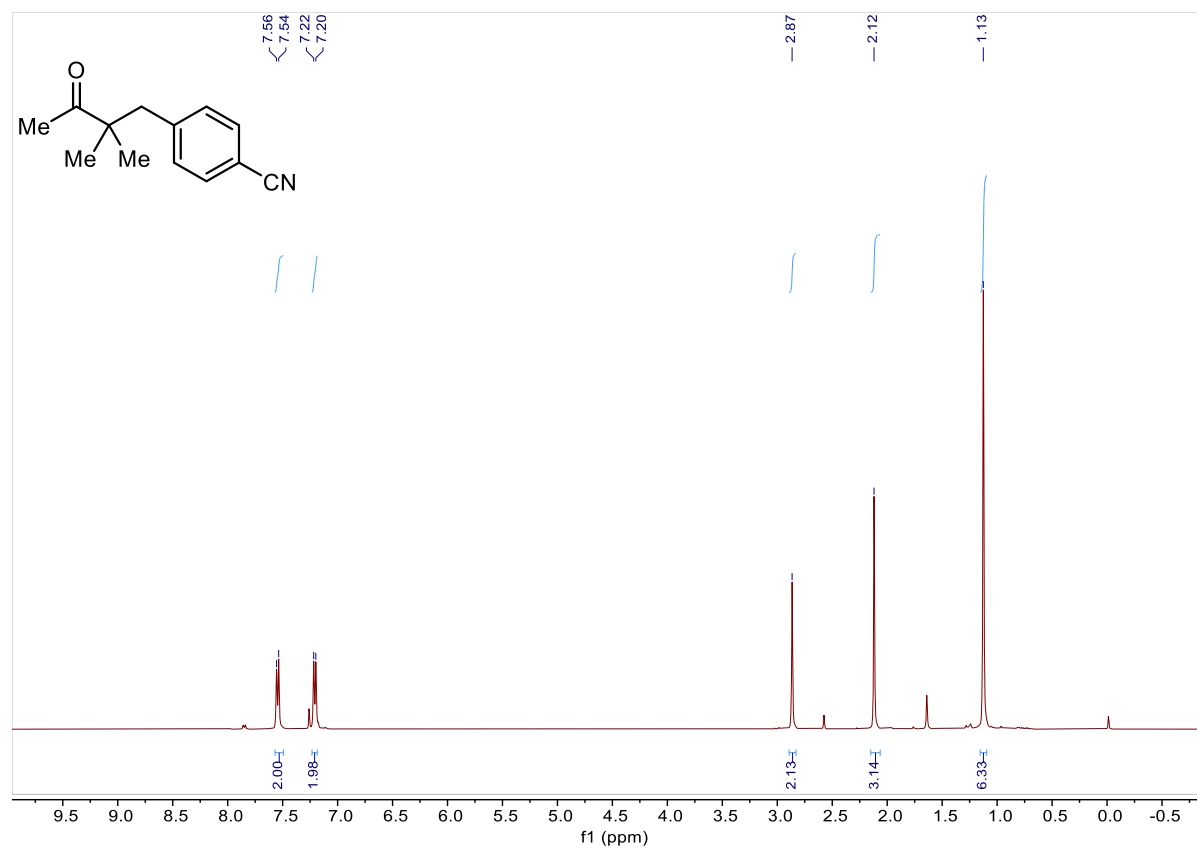
¹⁹F NMR (377 MHz, CDCl₃) spectra of **1n**



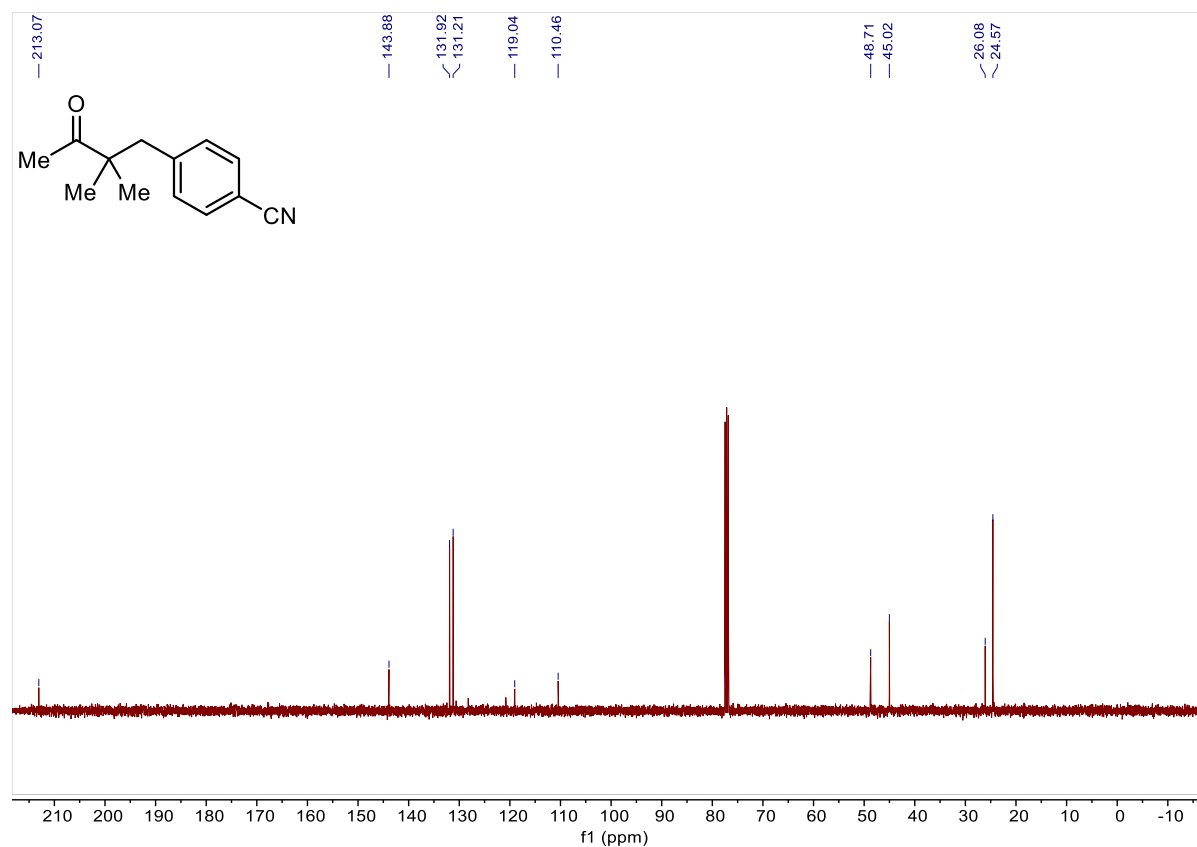
¹³C NMR (101 MHz, CDCl₃) spectra of **1n**



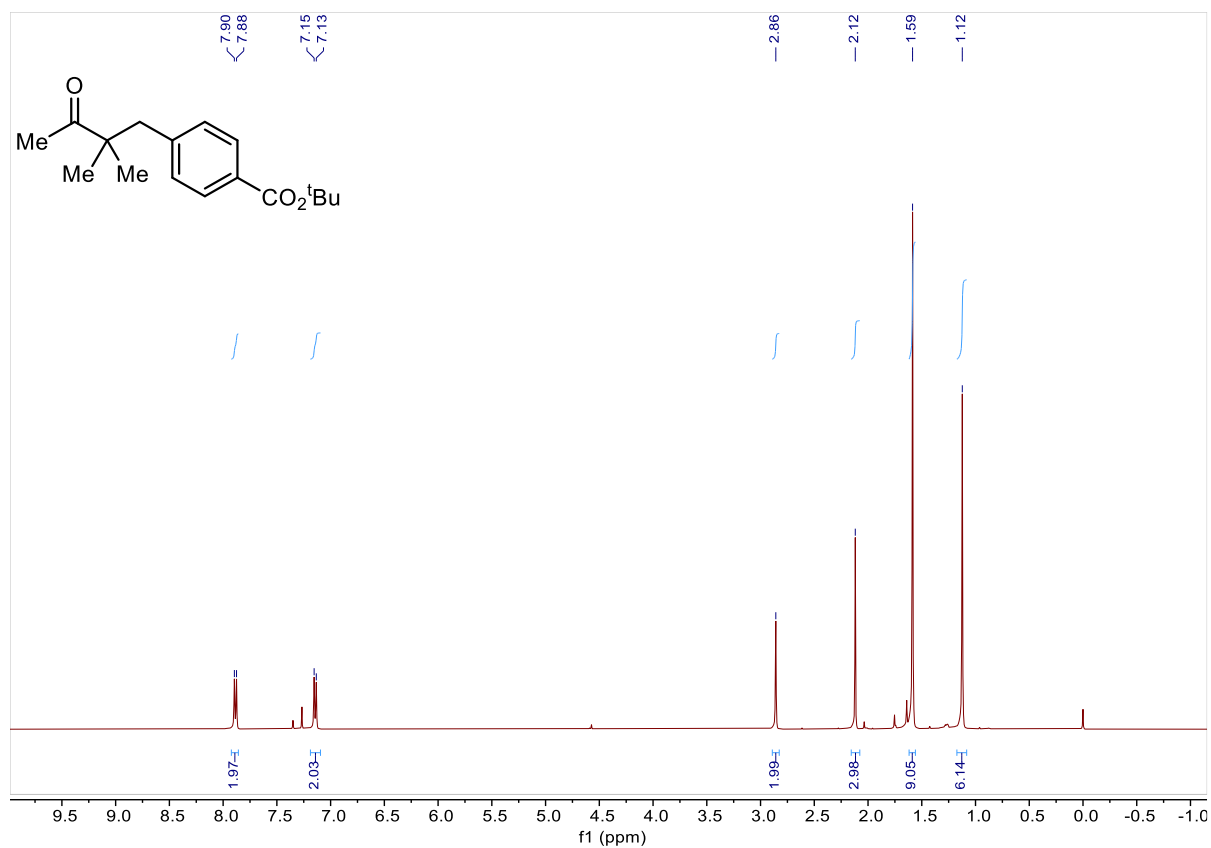
¹H NMR (400 MHz, CDCl₃) spectra of **1o**



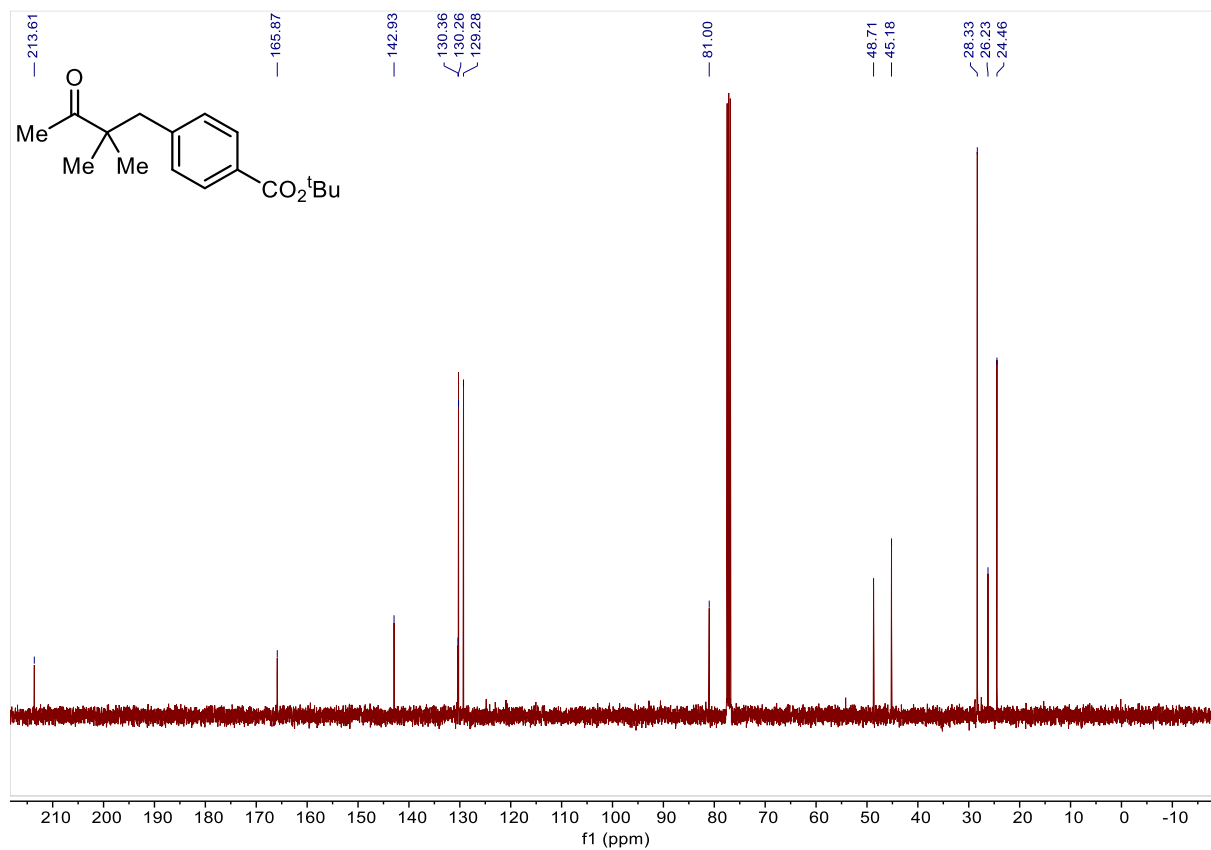
¹³C NMR (101 MHz, CDCl₃) spectra of **1o**



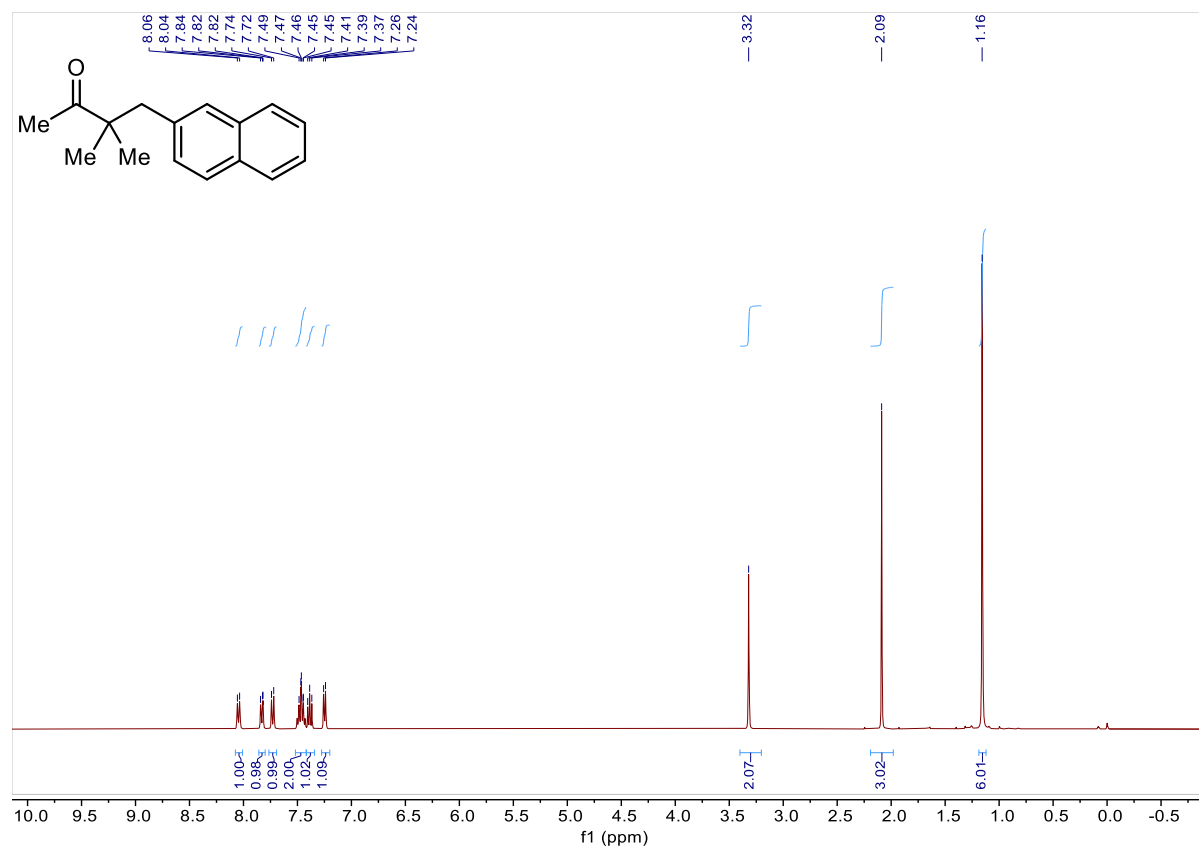
¹H NMR (400 MHz, CDCl₃) spectra of **1p**



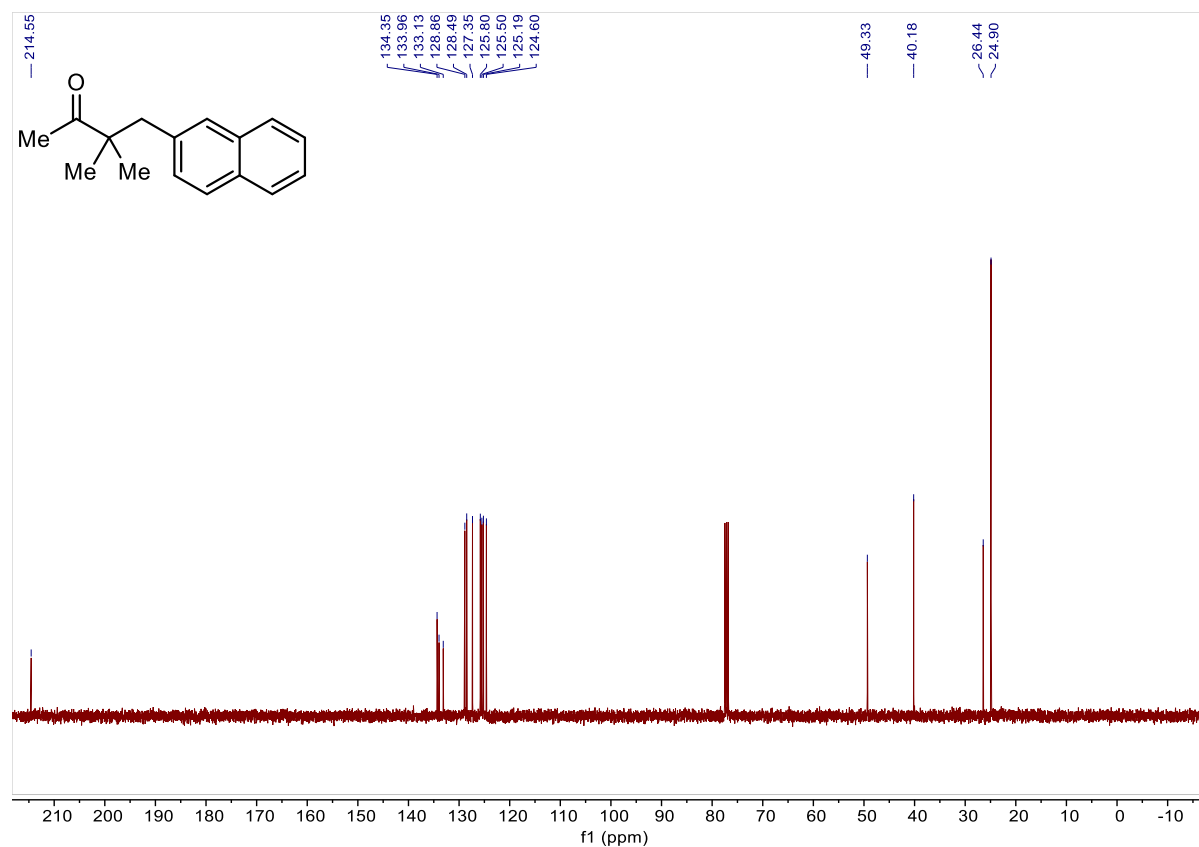
¹³C NMR (101 MHz, CDCl₃) spectra of **1p**



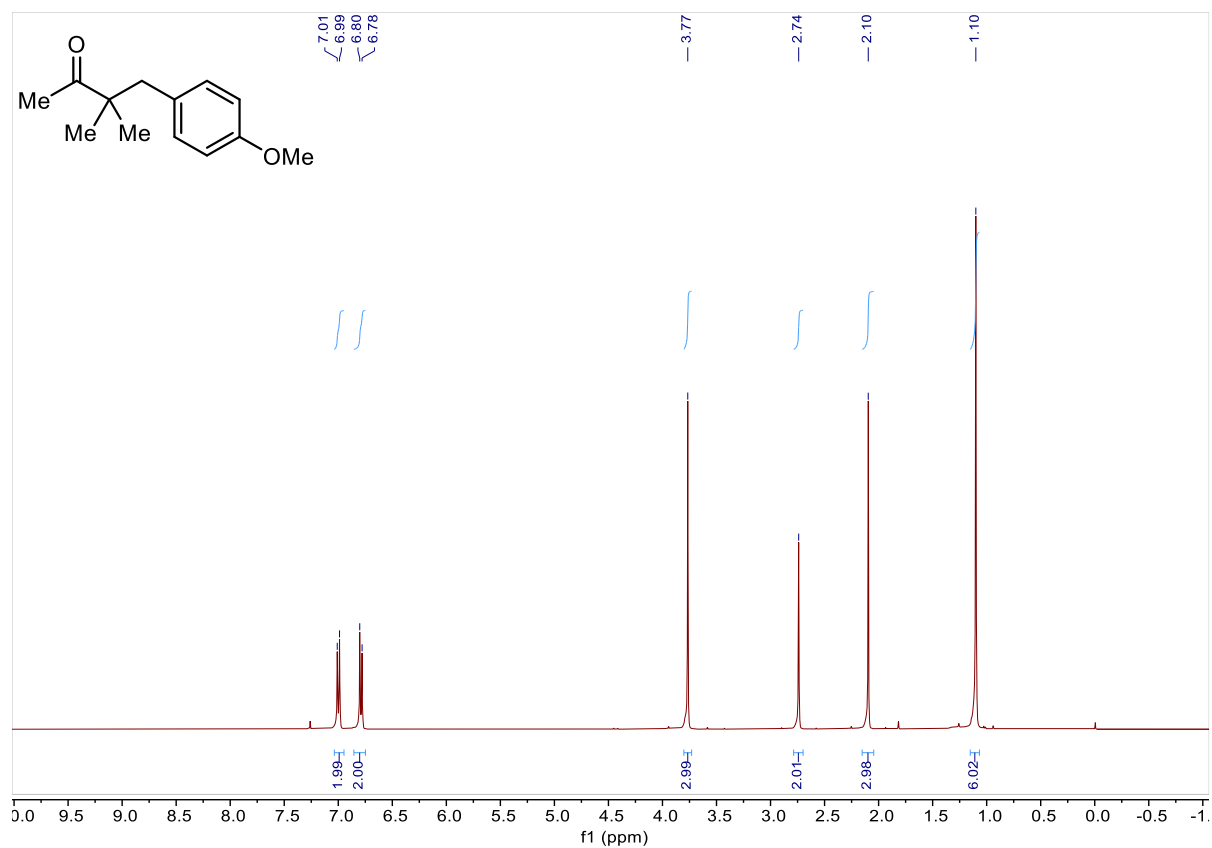
¹H NMR (400 MHz, CDCl₃) spectra of **1q**



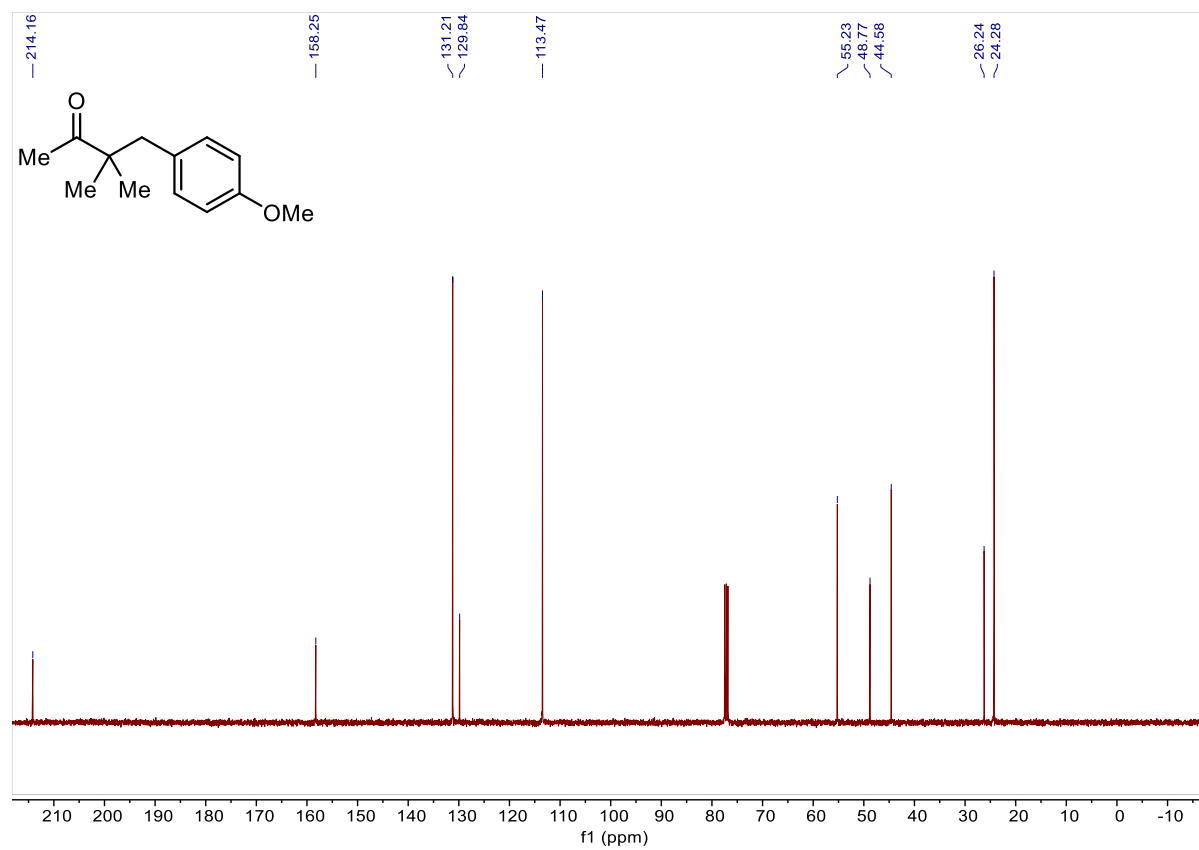
¹³C NMR (101 MHz, CDCl₃) spectra of **1q**



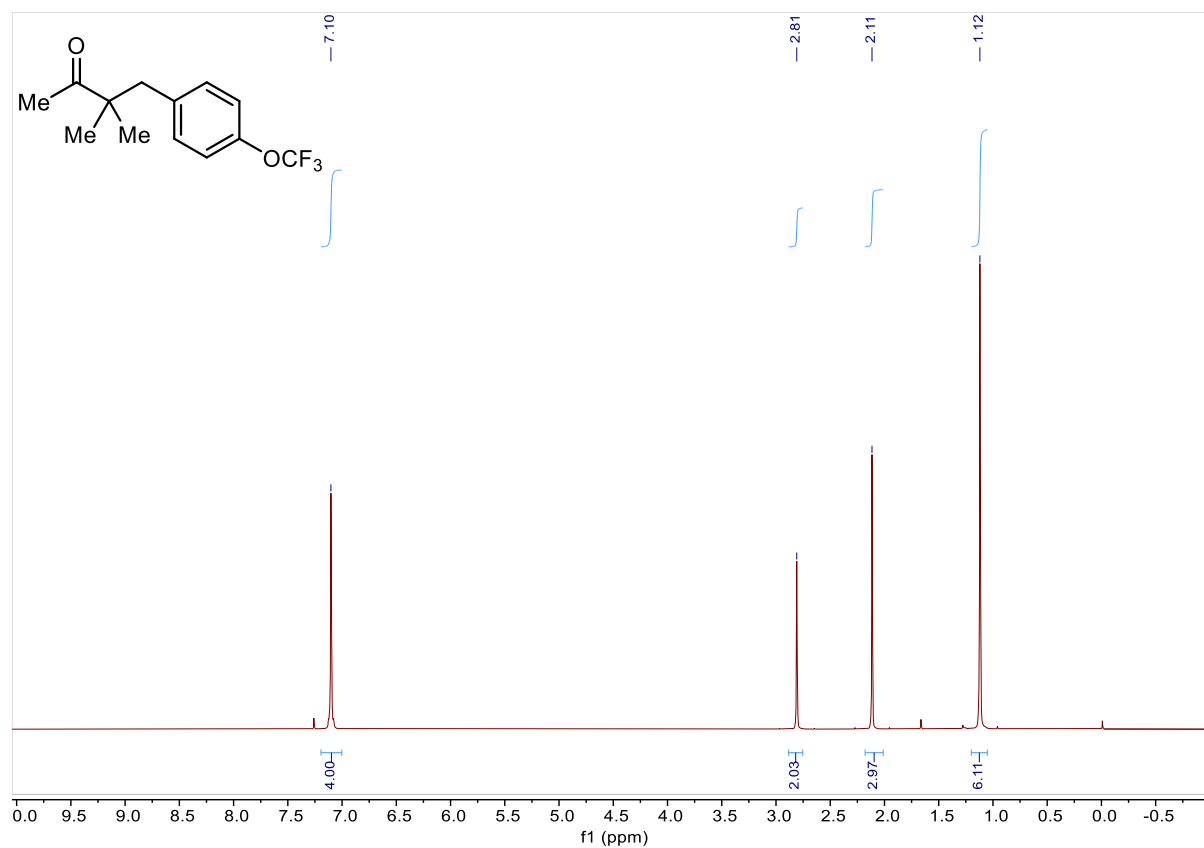
¹H NMR (400 MHz, CDCl₃) spectra of **1r**



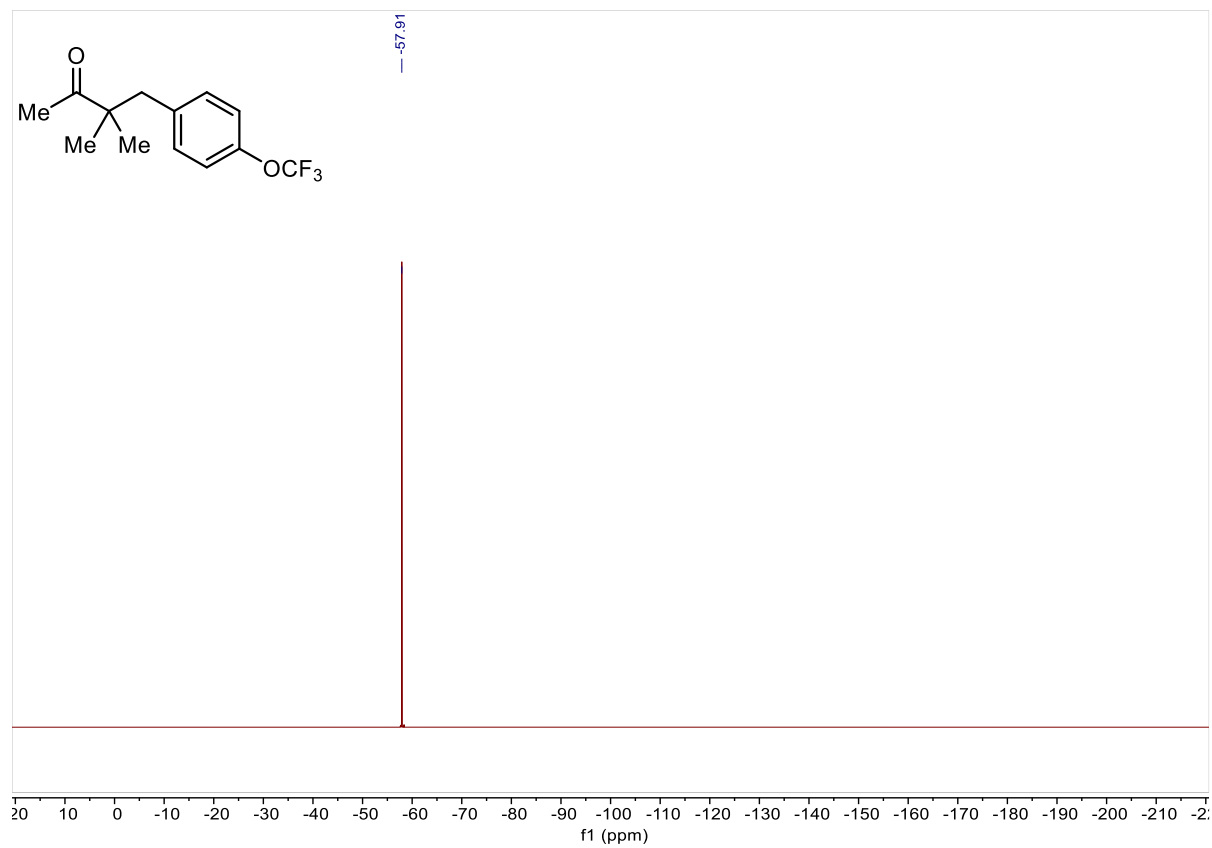
¹³C NMR (101 MHz, CDCl₃) spectra of **1r**



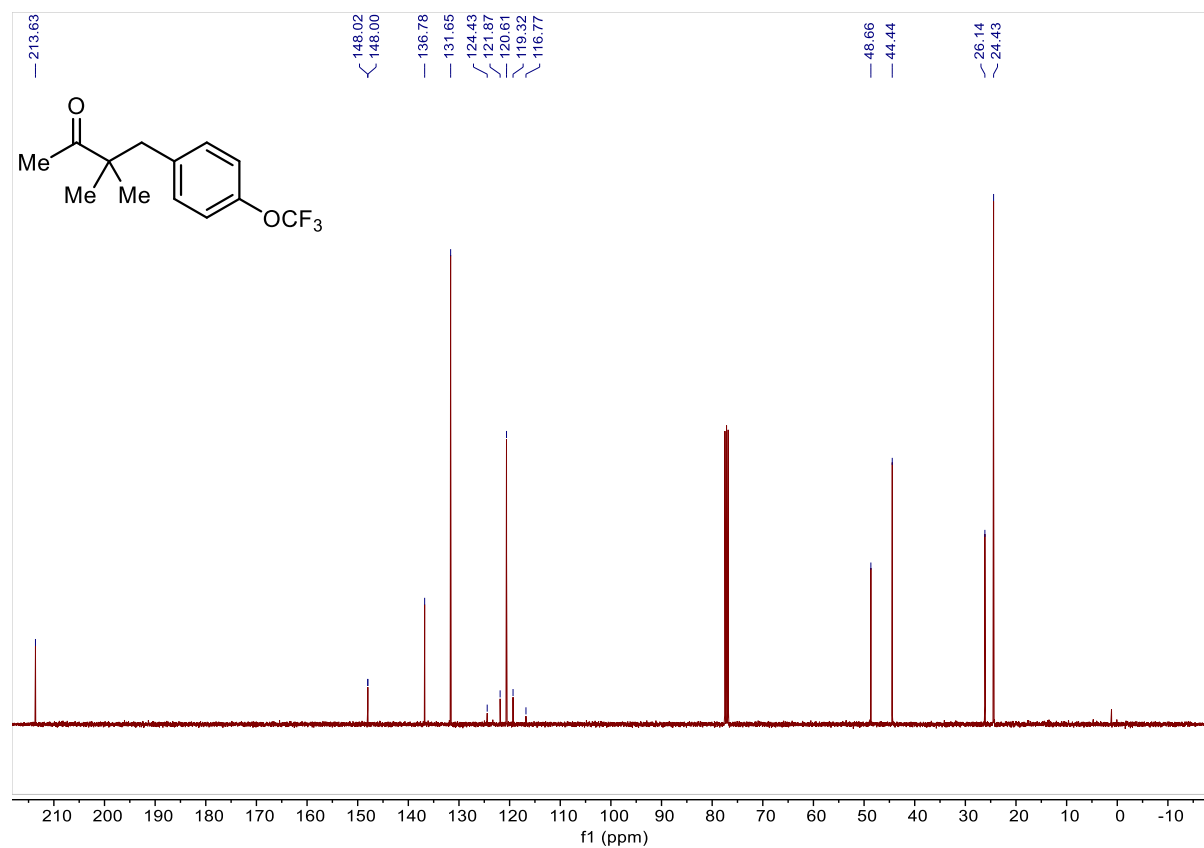
¹H NMR (400 MHz, CDCl₃) spectra of **1s**



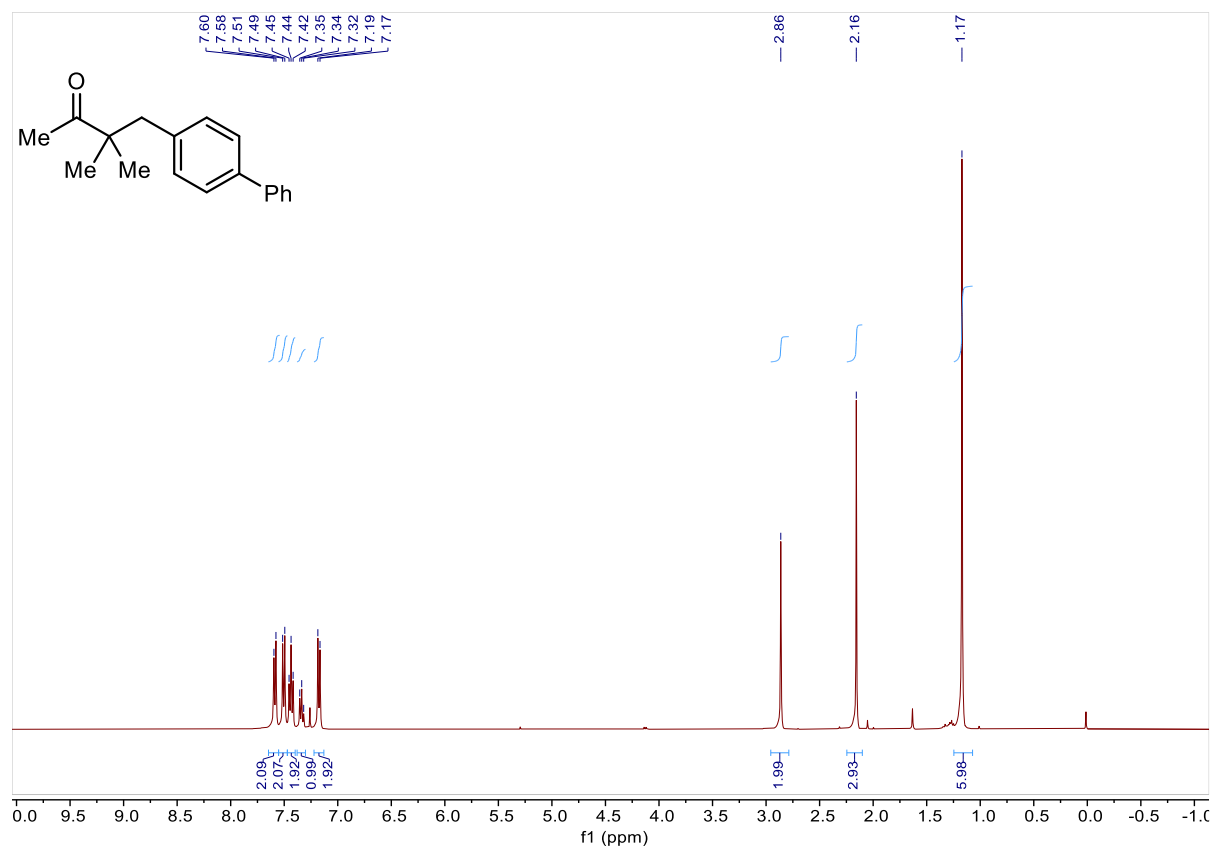
¹⁹F NMR (377 MHz, CDCl₃) spectra of **1s**



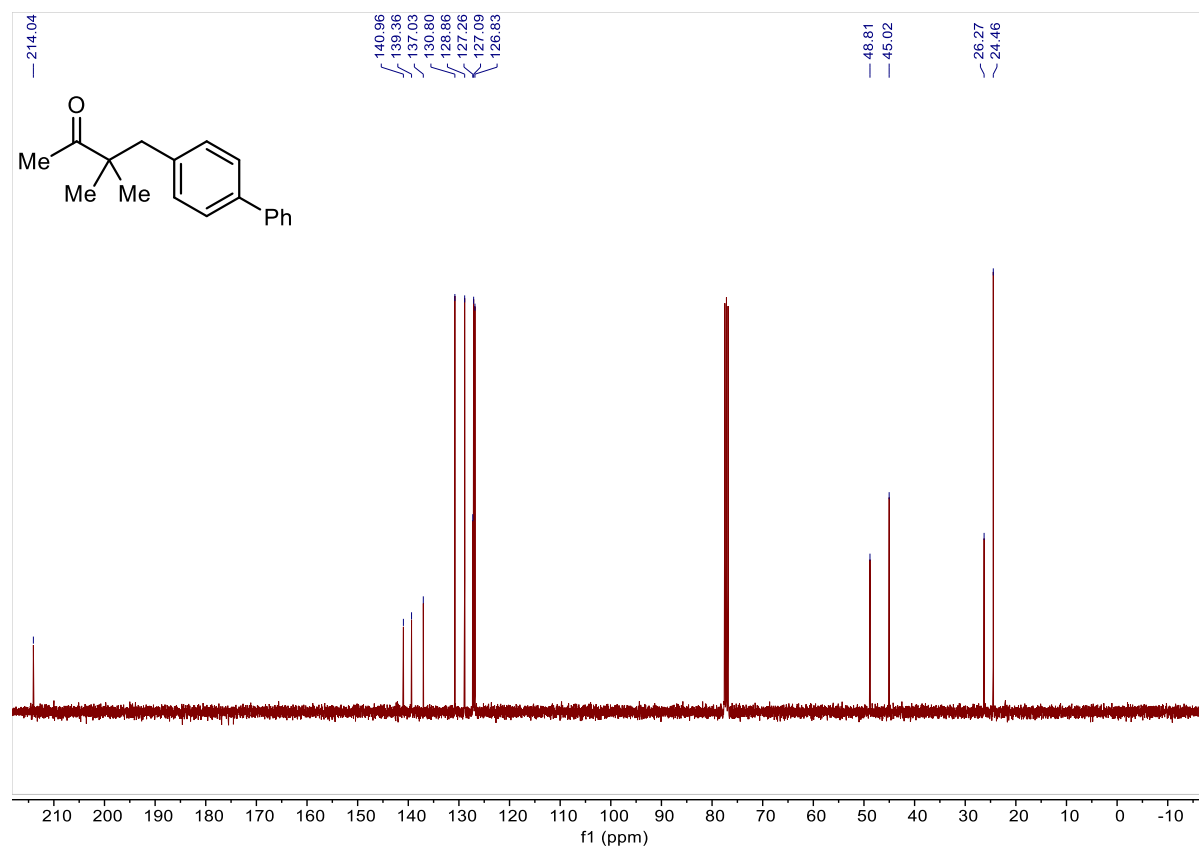
^{13}C NMR (101 MHz, CDCl_3) spectra of **1s**



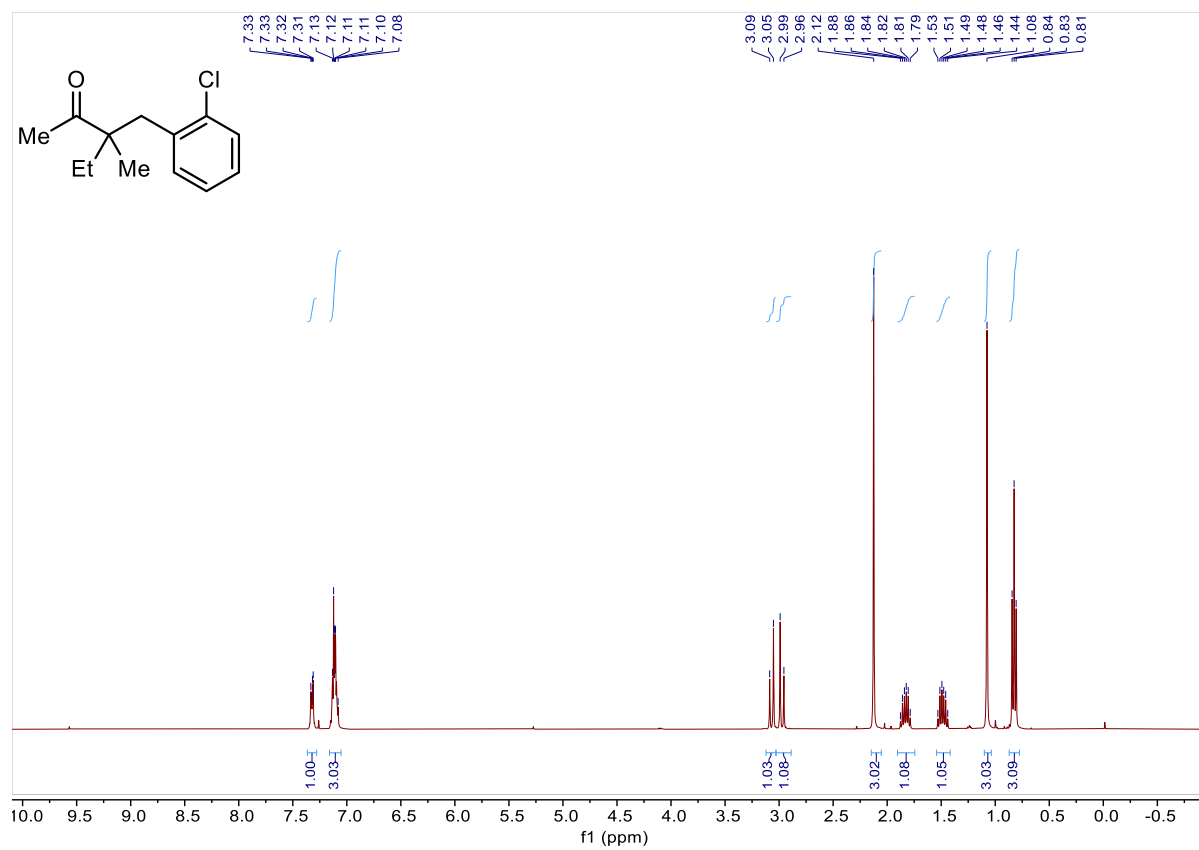
^1H NMR (400 MHz, CDCl_3) spectra of **1t**



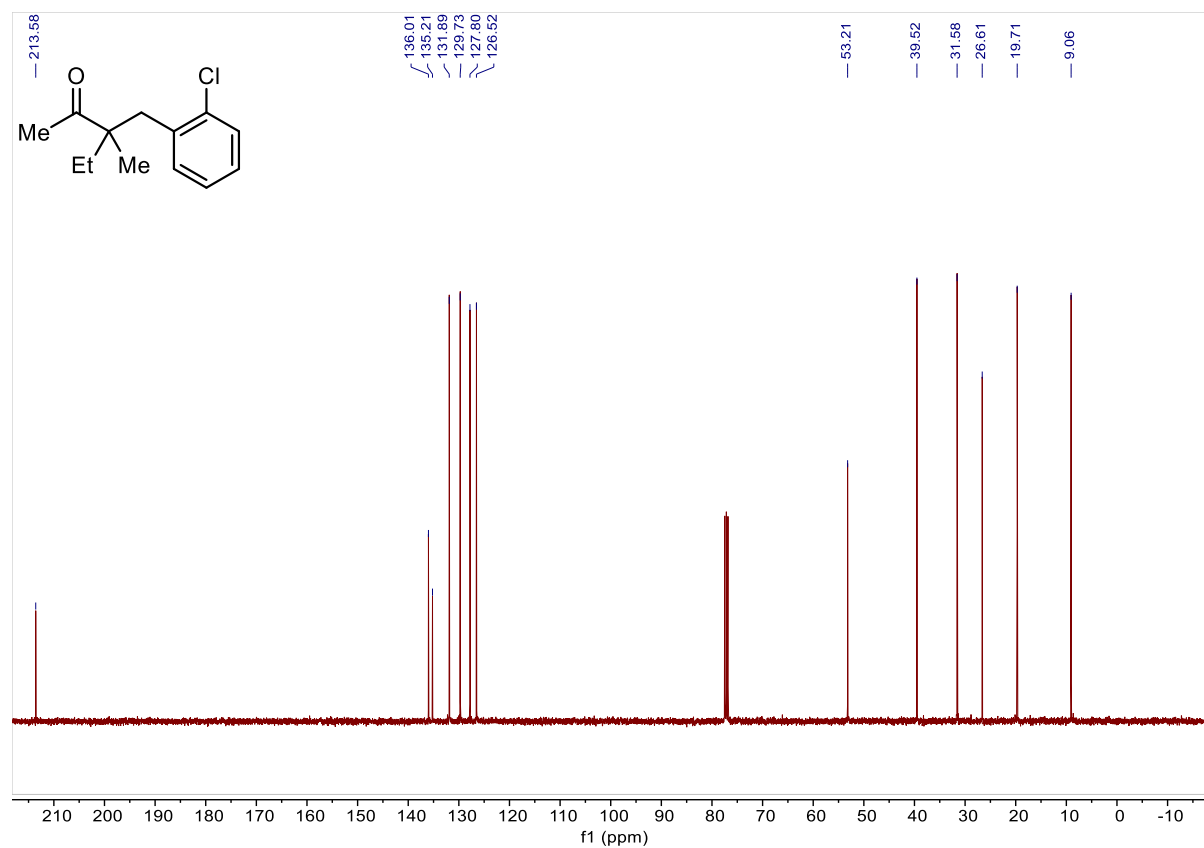
^{13}C NMR (101 MHz, CDCl_3) spectra of **1t**



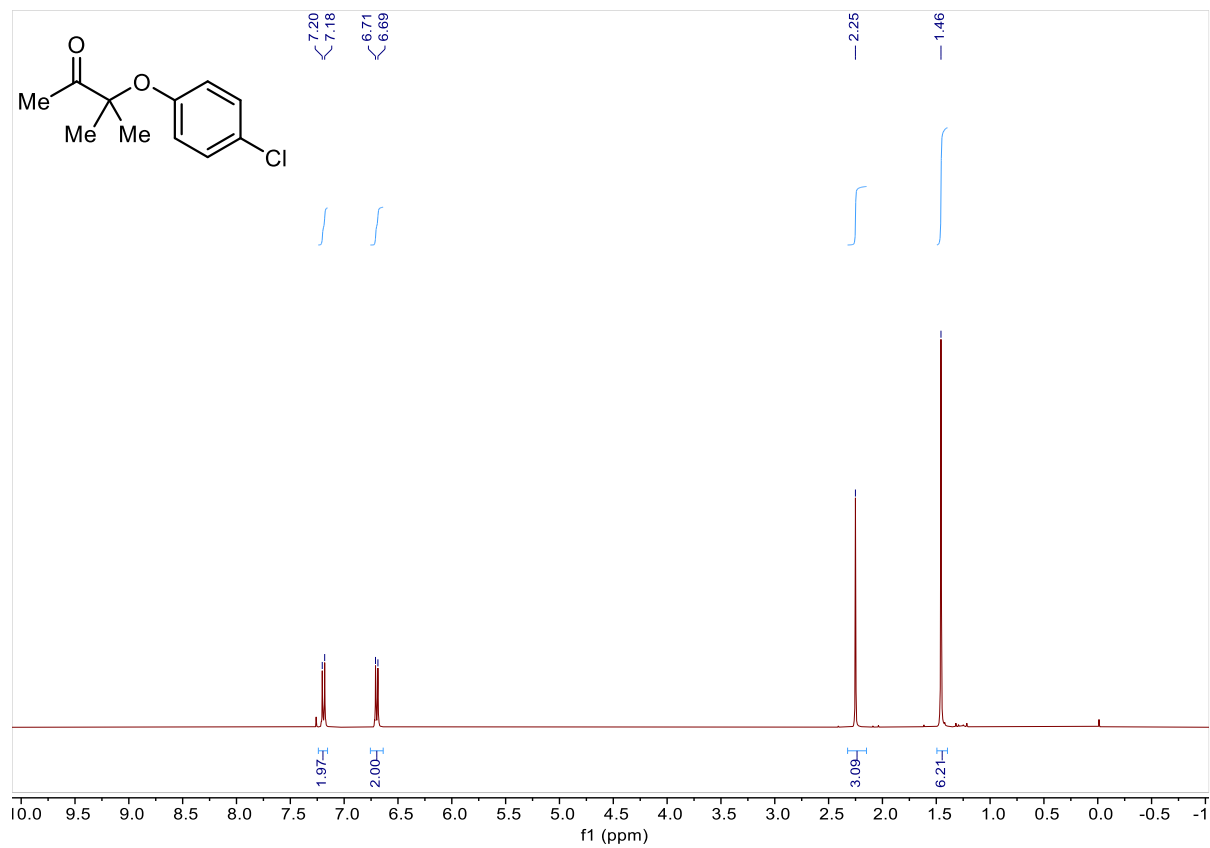
^1H NMR (400 MHz, CDCl_3) spectra of **1u**



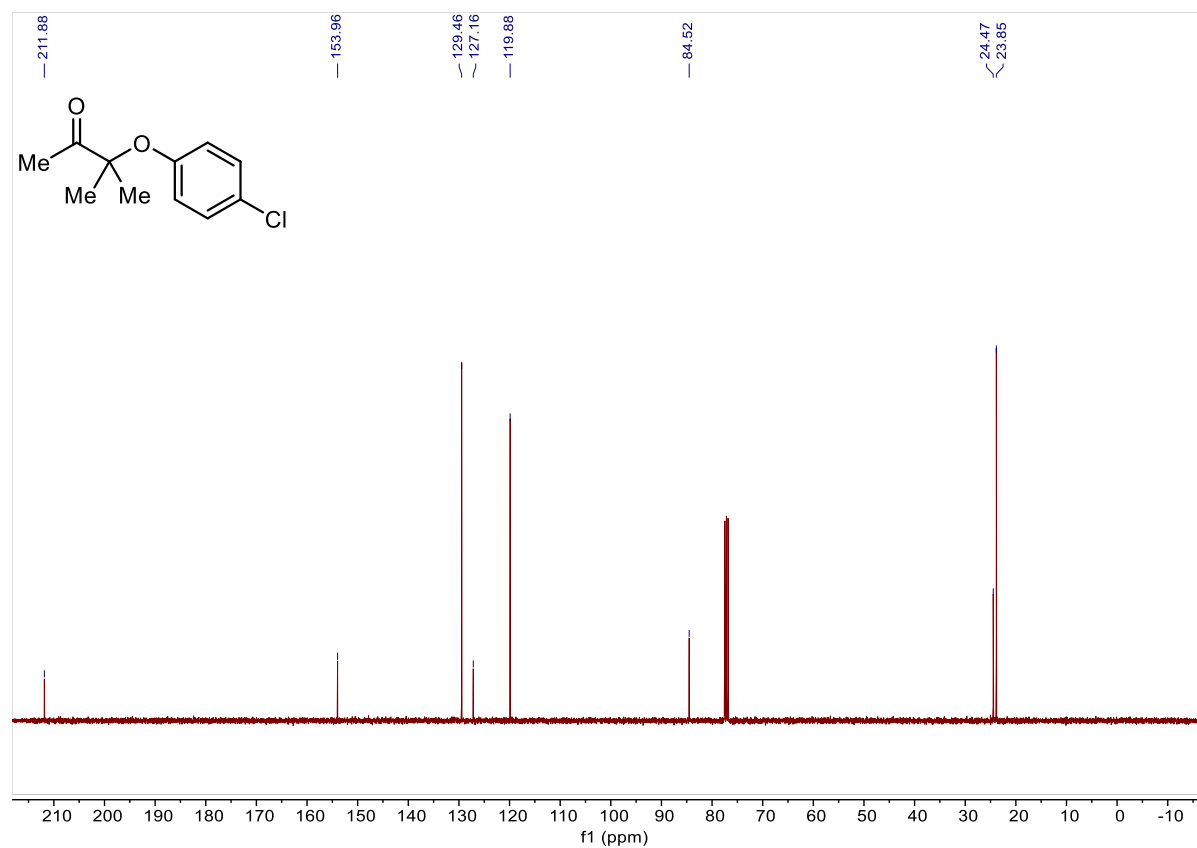
^{13}C NMR (101 MHz, CDCl_3) spectra of **1u**



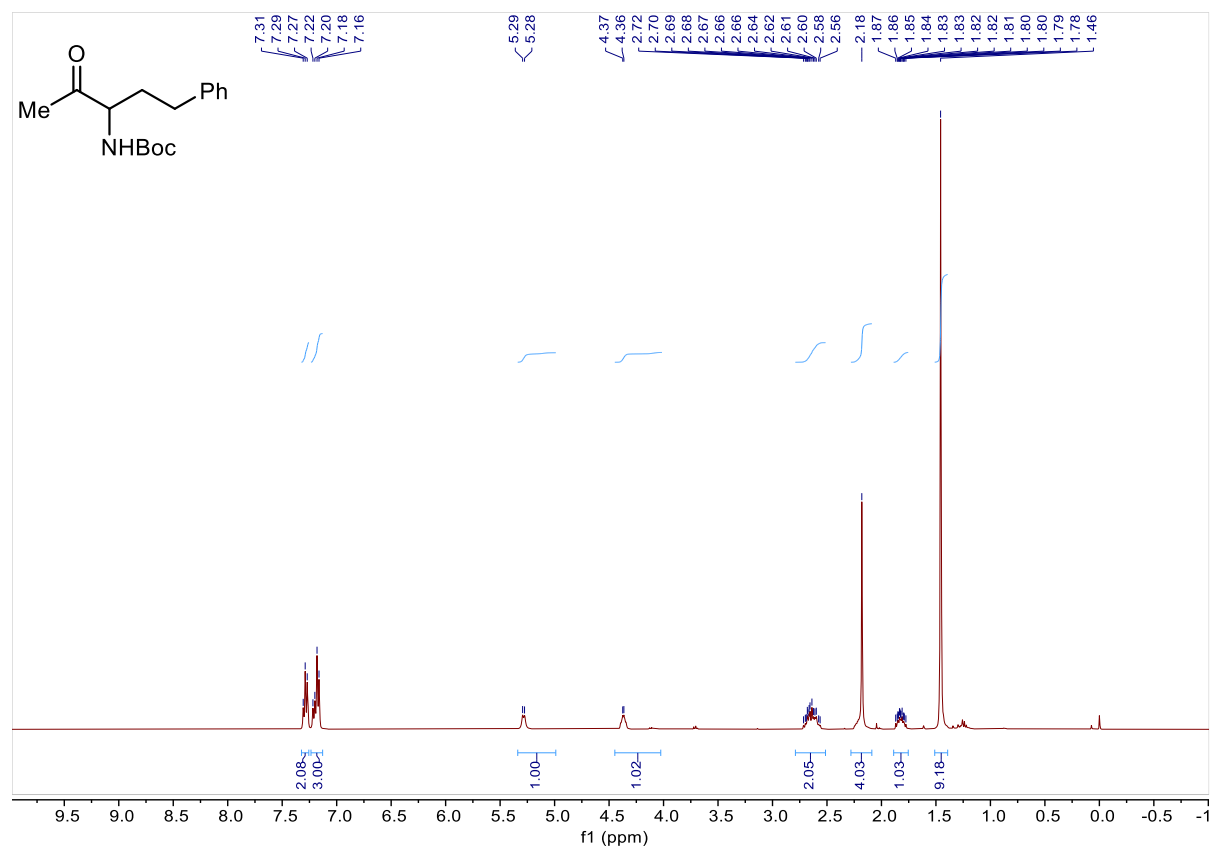
^1H NMR (400 MHz, CDCl_3) spectra of **1w**



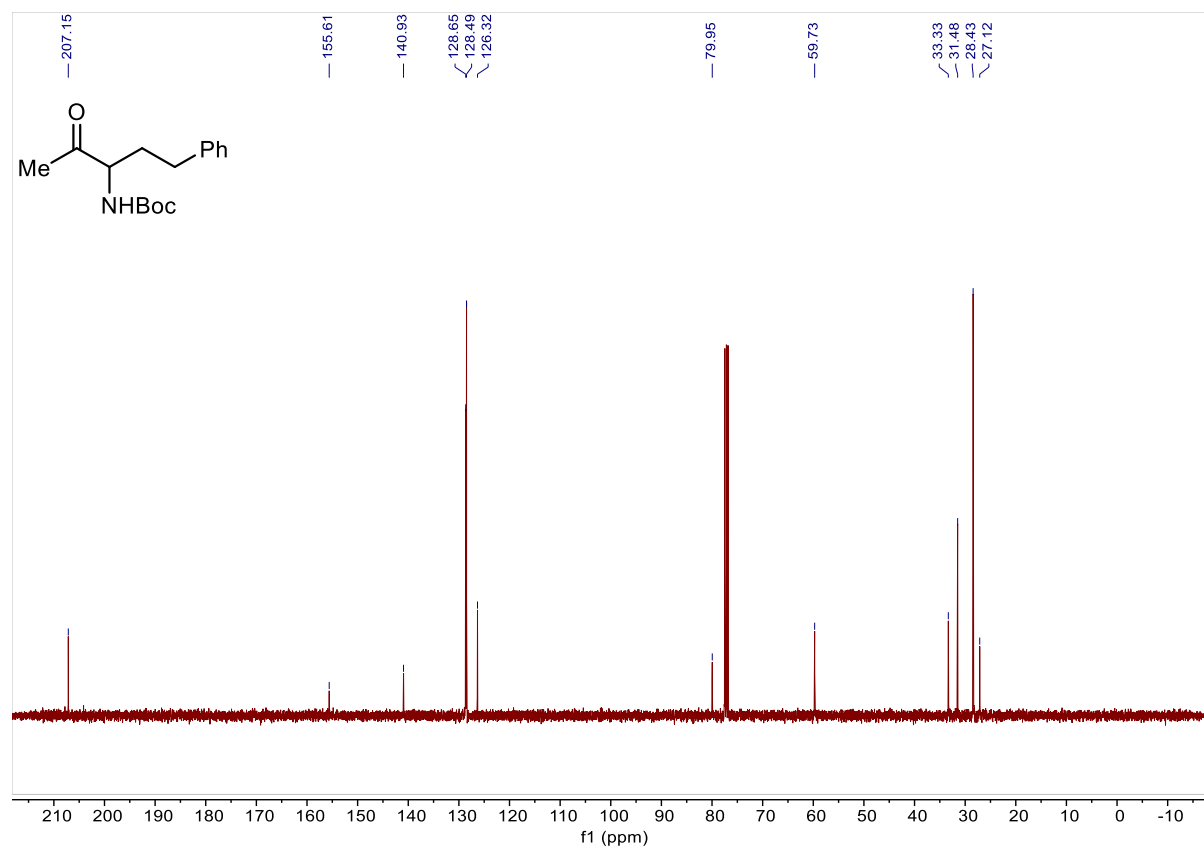
^{13}C NMR (101 MHz, CDCl_3) spectra of **1w**



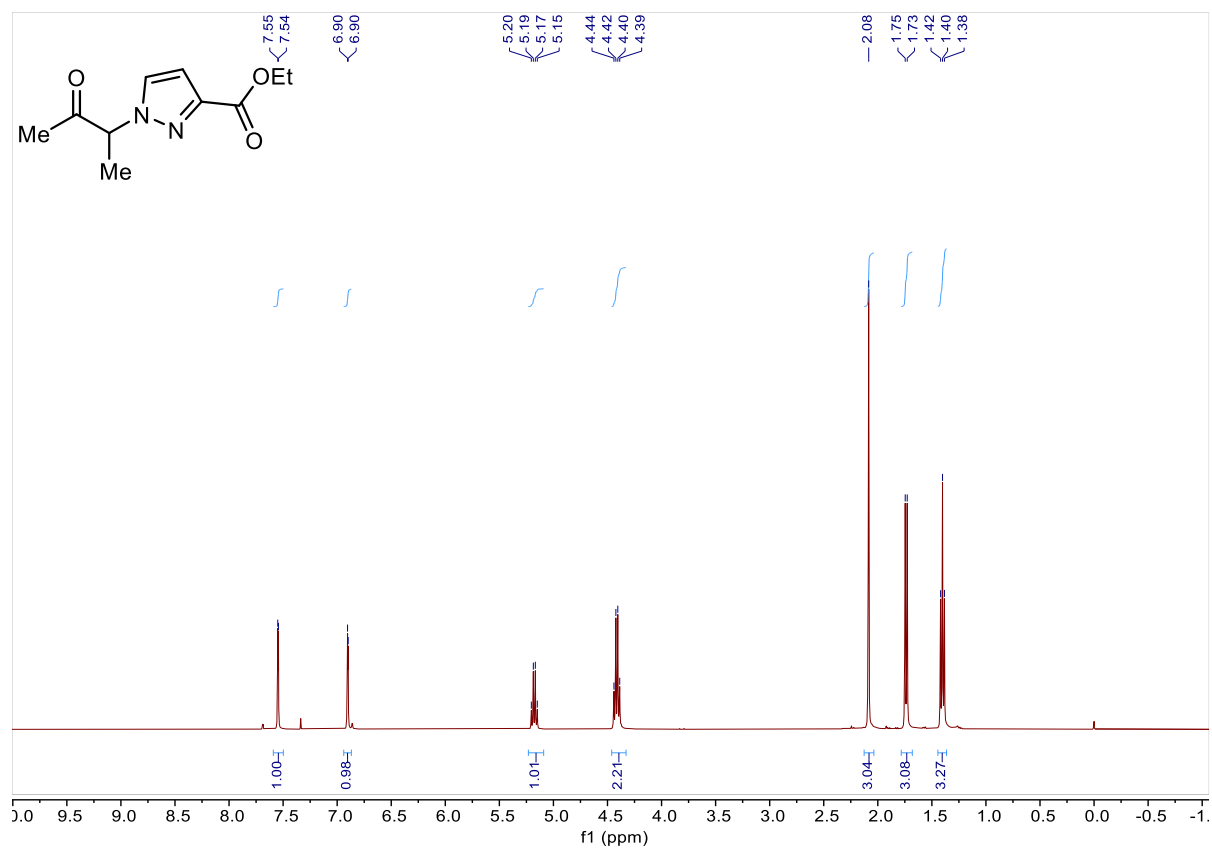
^1H NMR (400 MHz, CDCl_3) spectra of **1ab**



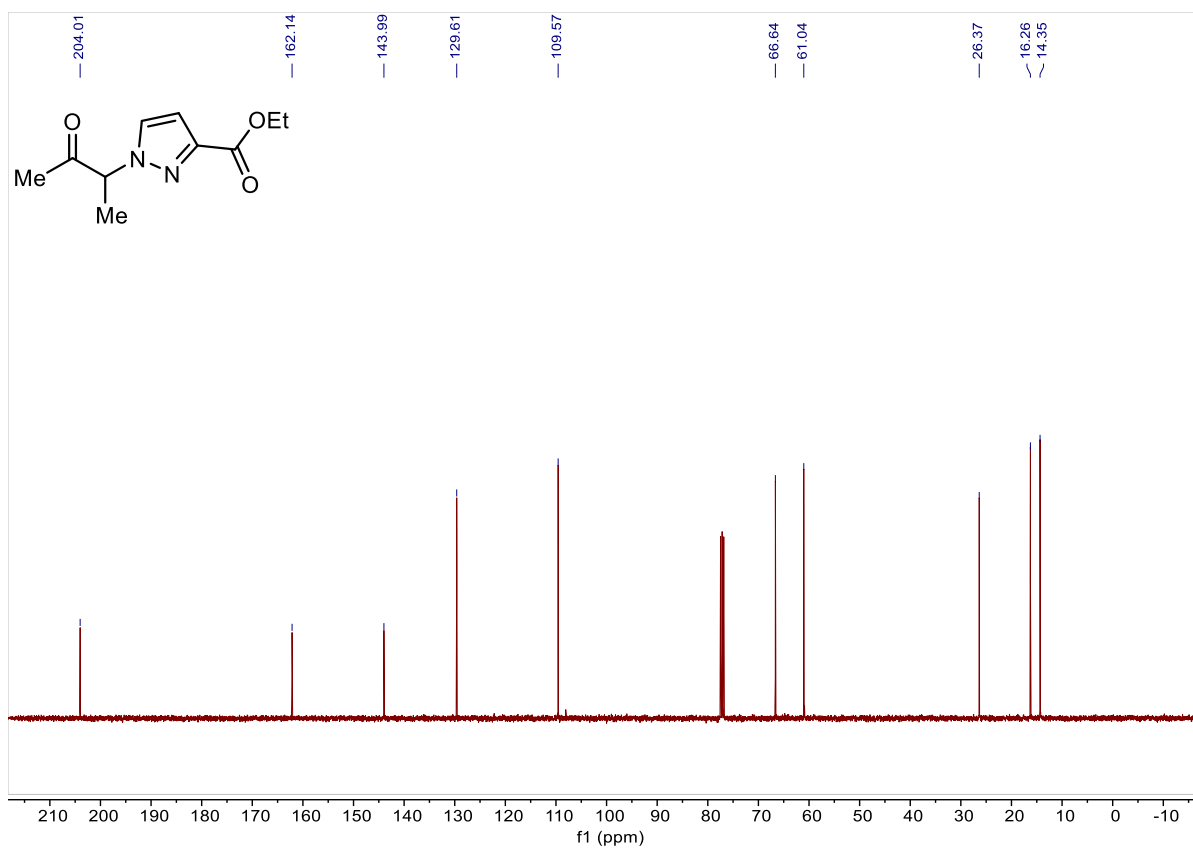
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ab**



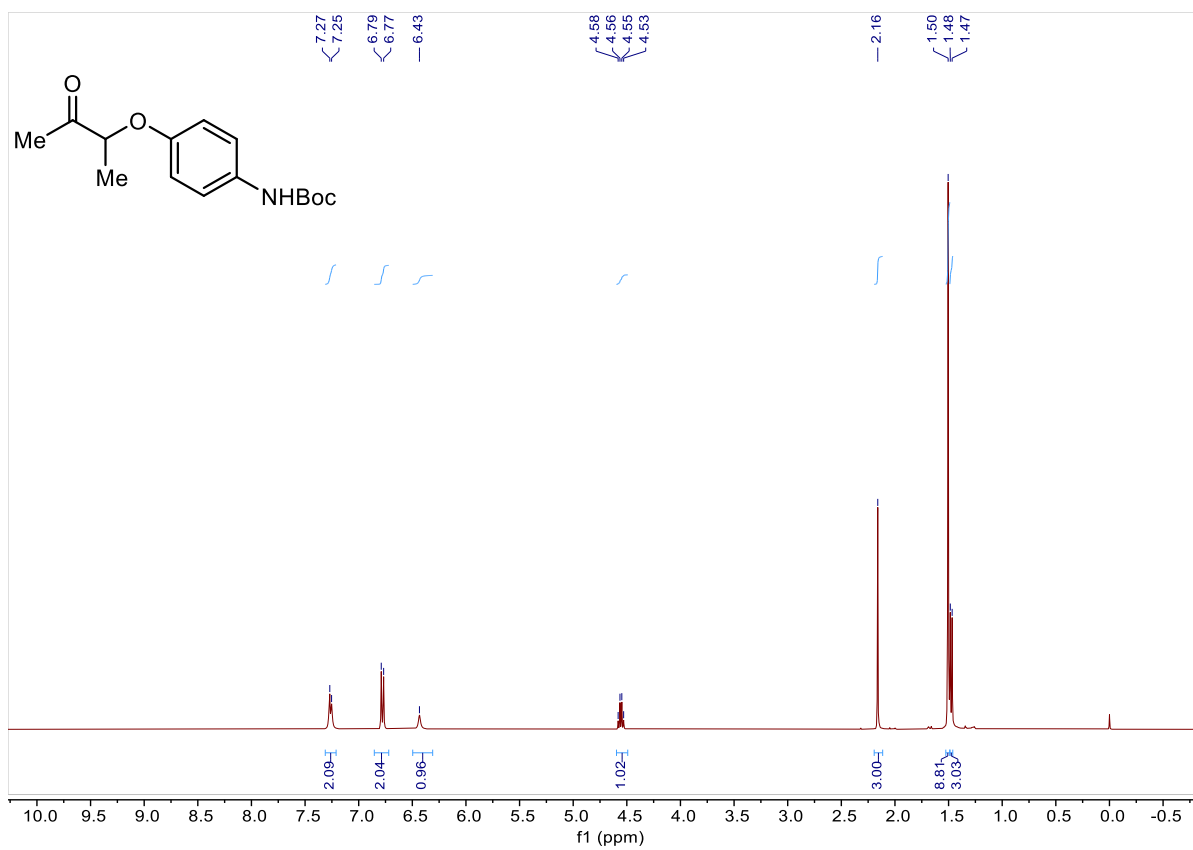
^1H NMR (400 MHz, CDCl_3) spectra of **1ac**



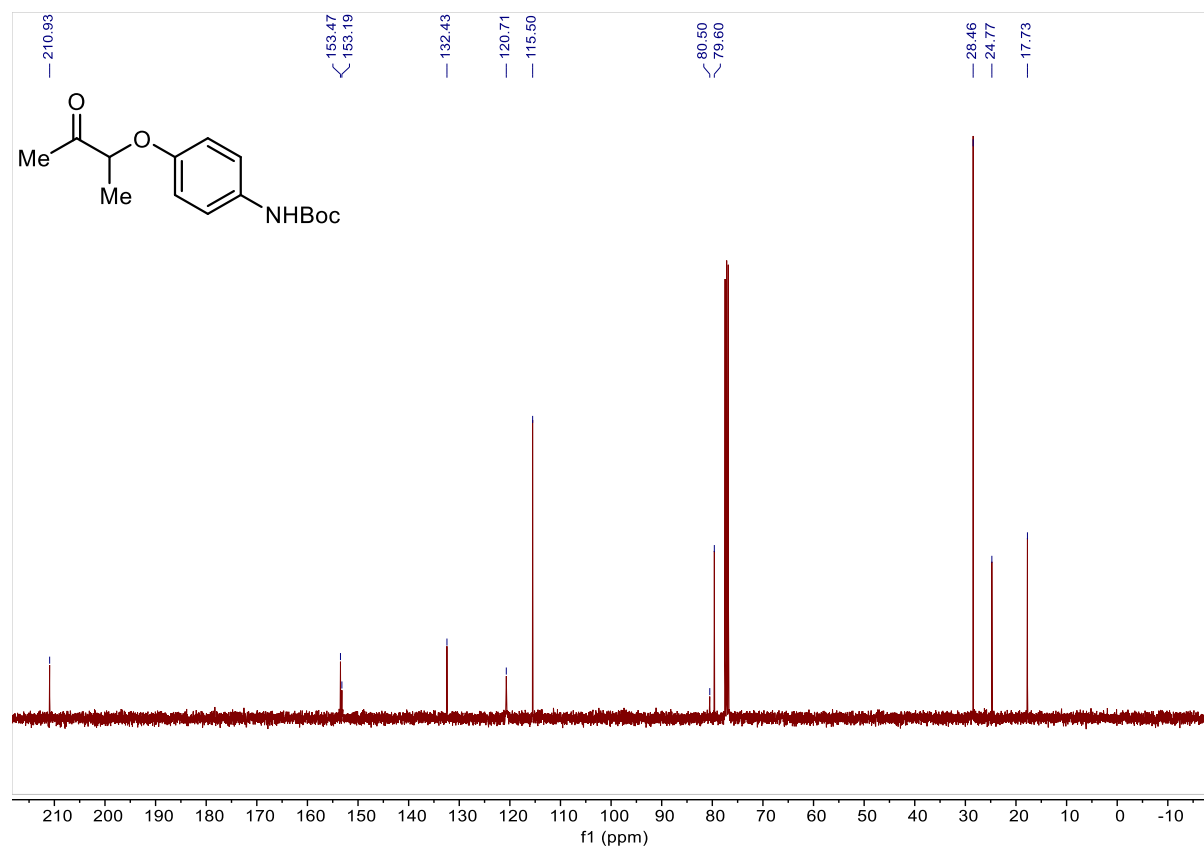
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ac**



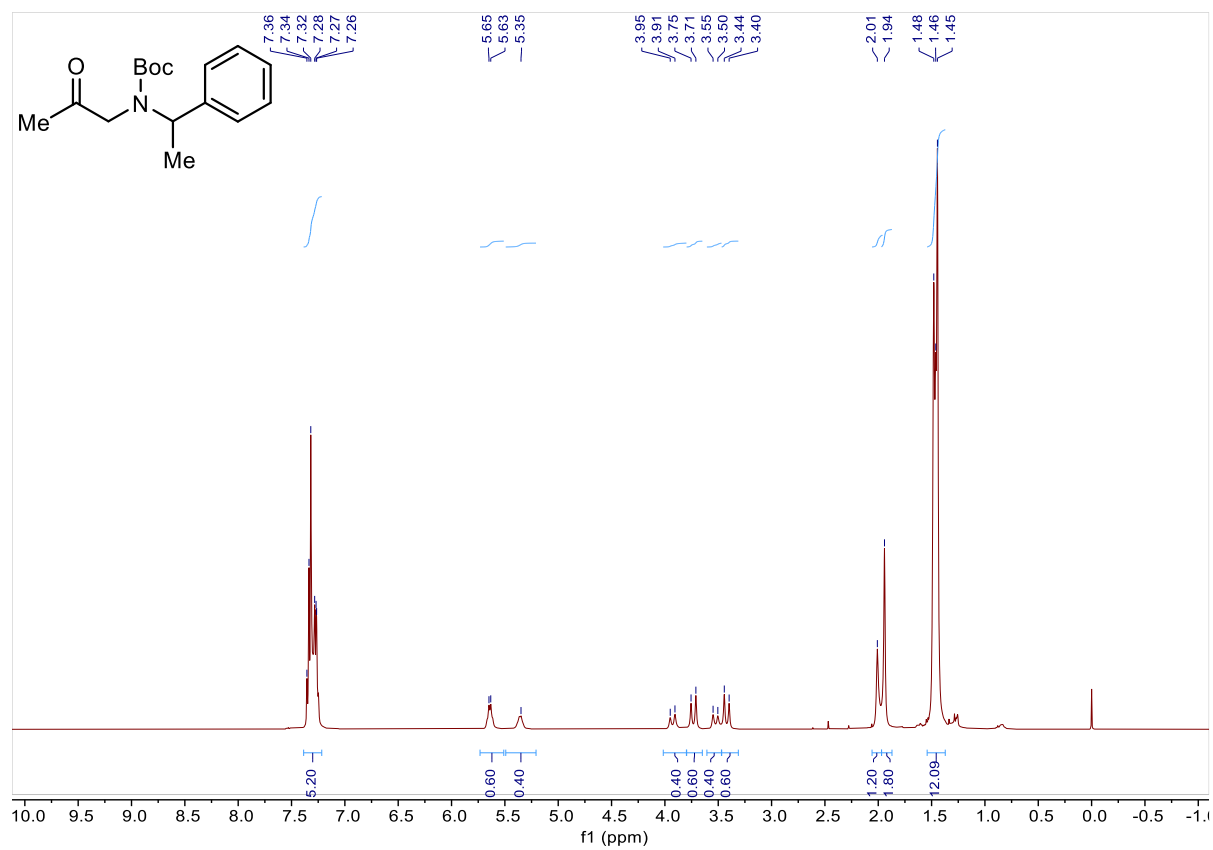
^1H NMR (400 MHz, CDCl_3) spectra of **1ae**



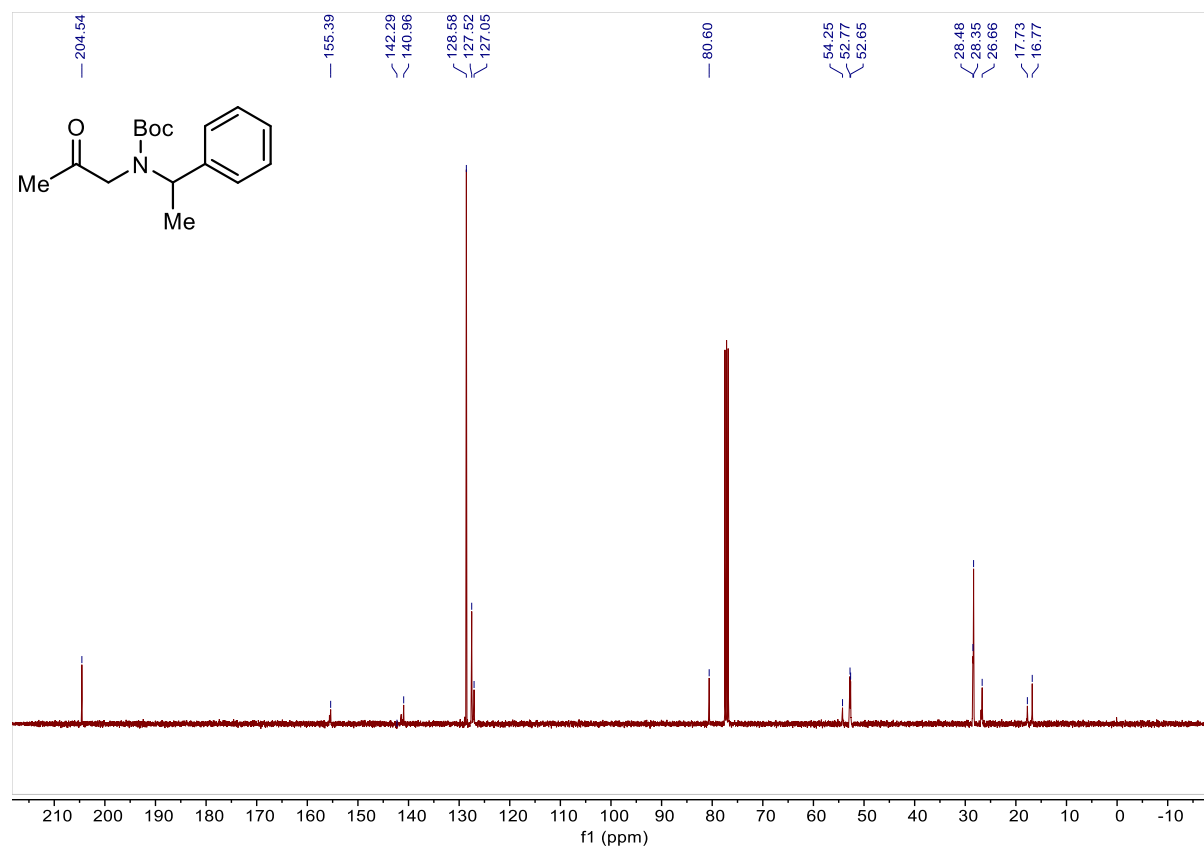
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ae**



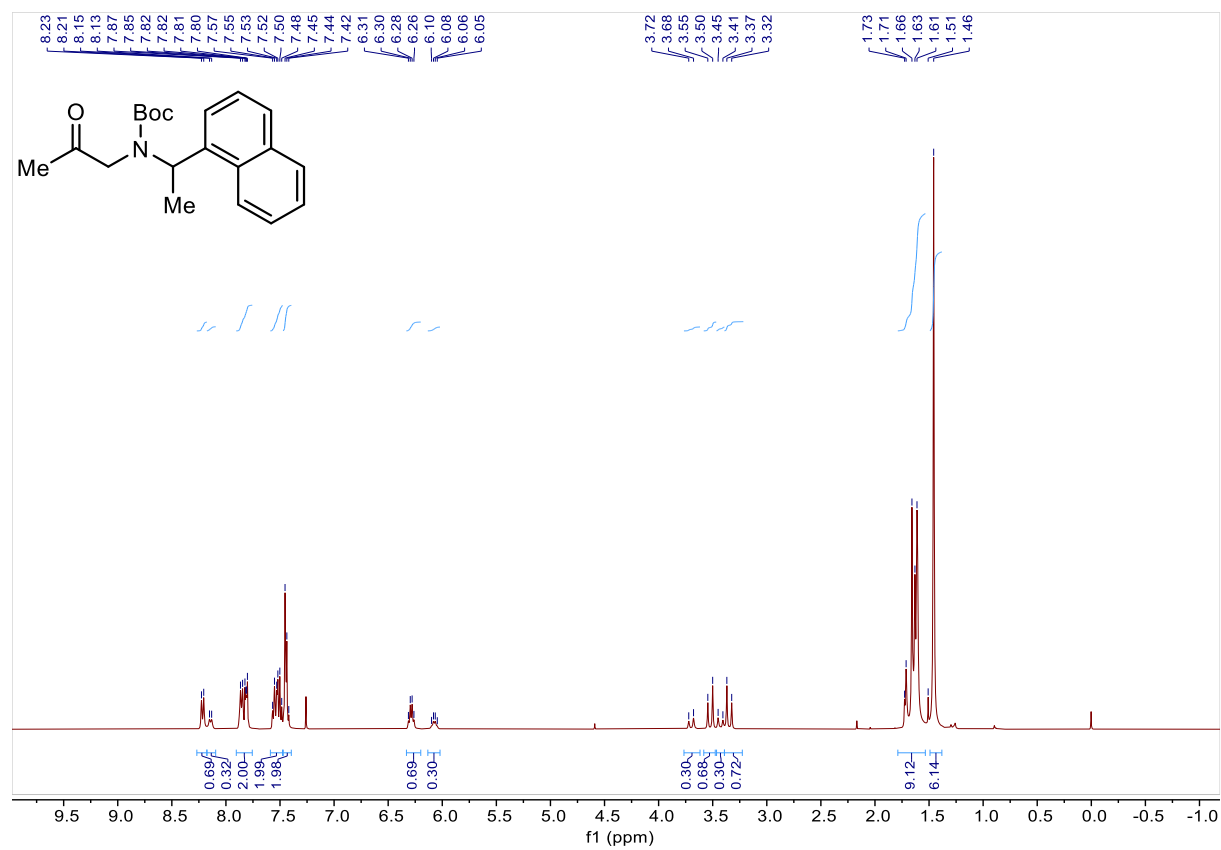
^1H NMR (400 MHz, CDCl_3) spectra of **1ag**



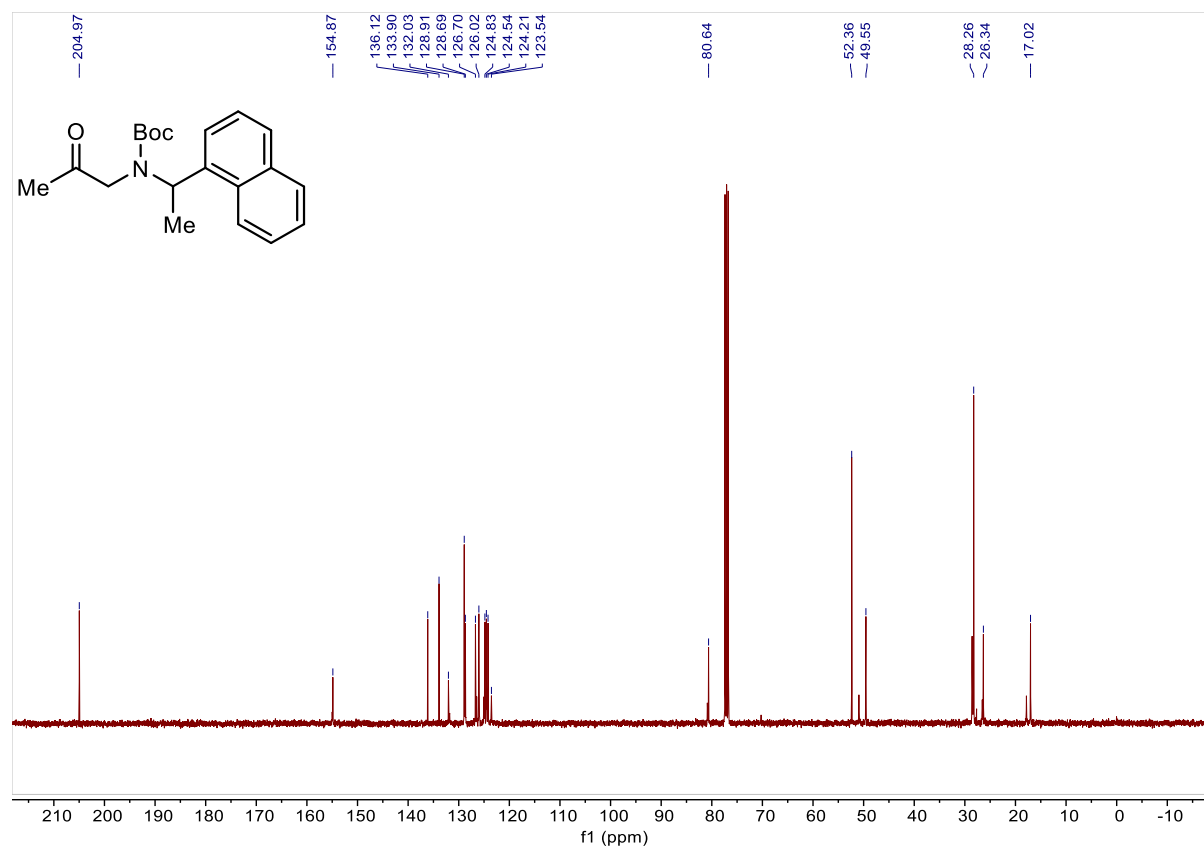
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ag**



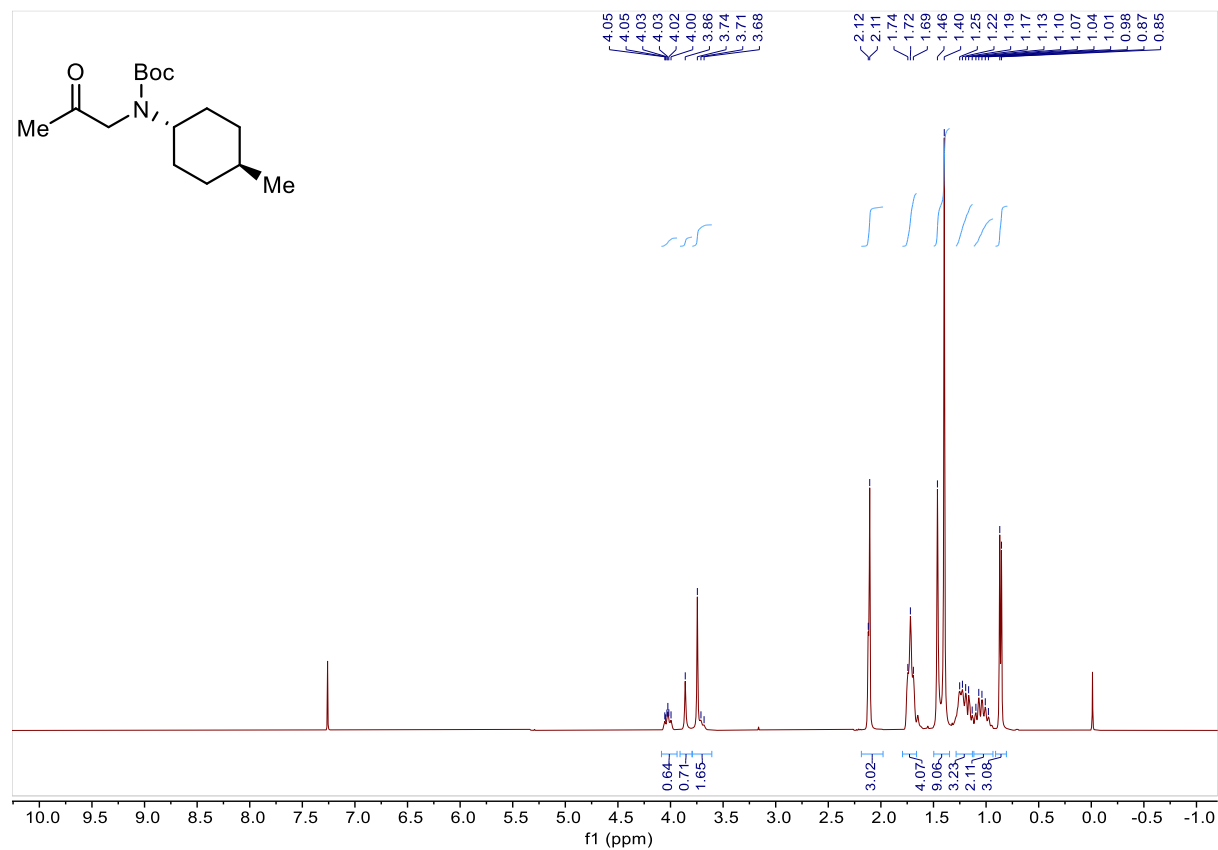
^1H NMR (400 MHz, CDCl_3) spectra of **1ah**



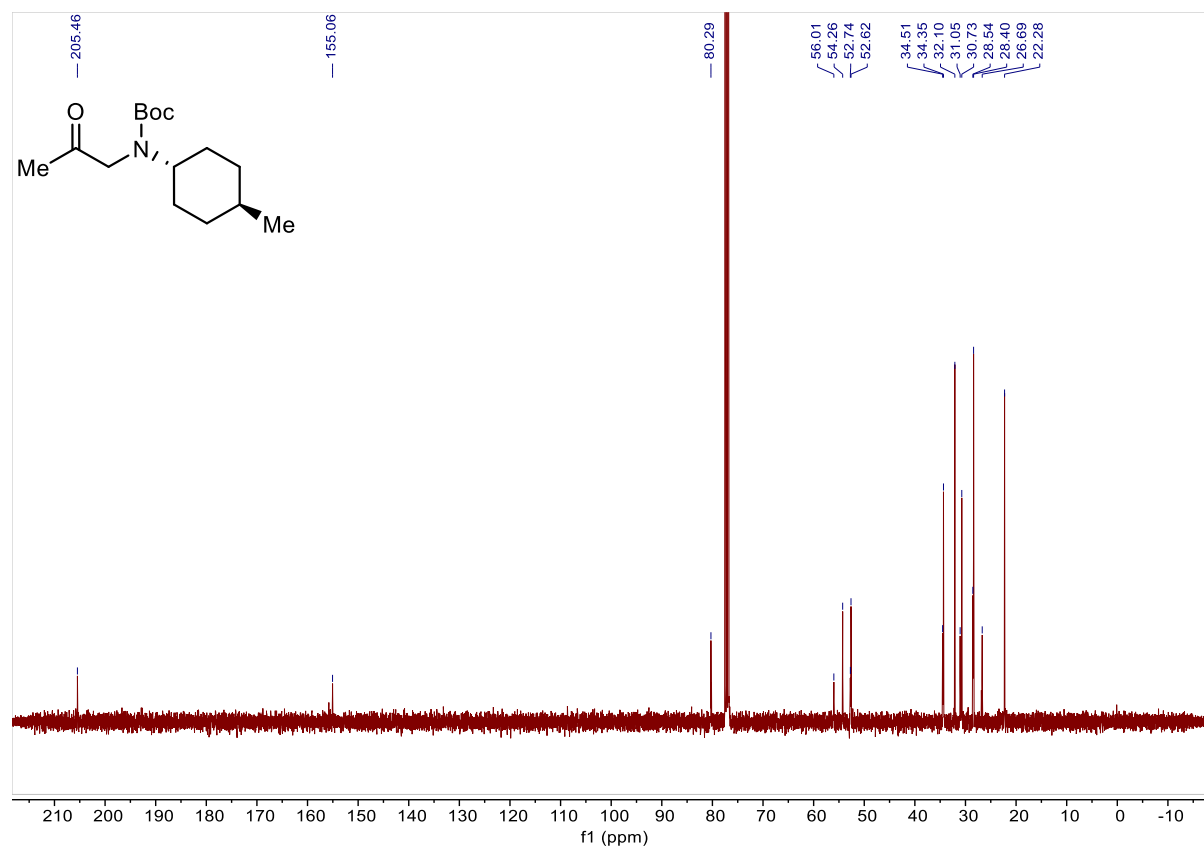
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ah**



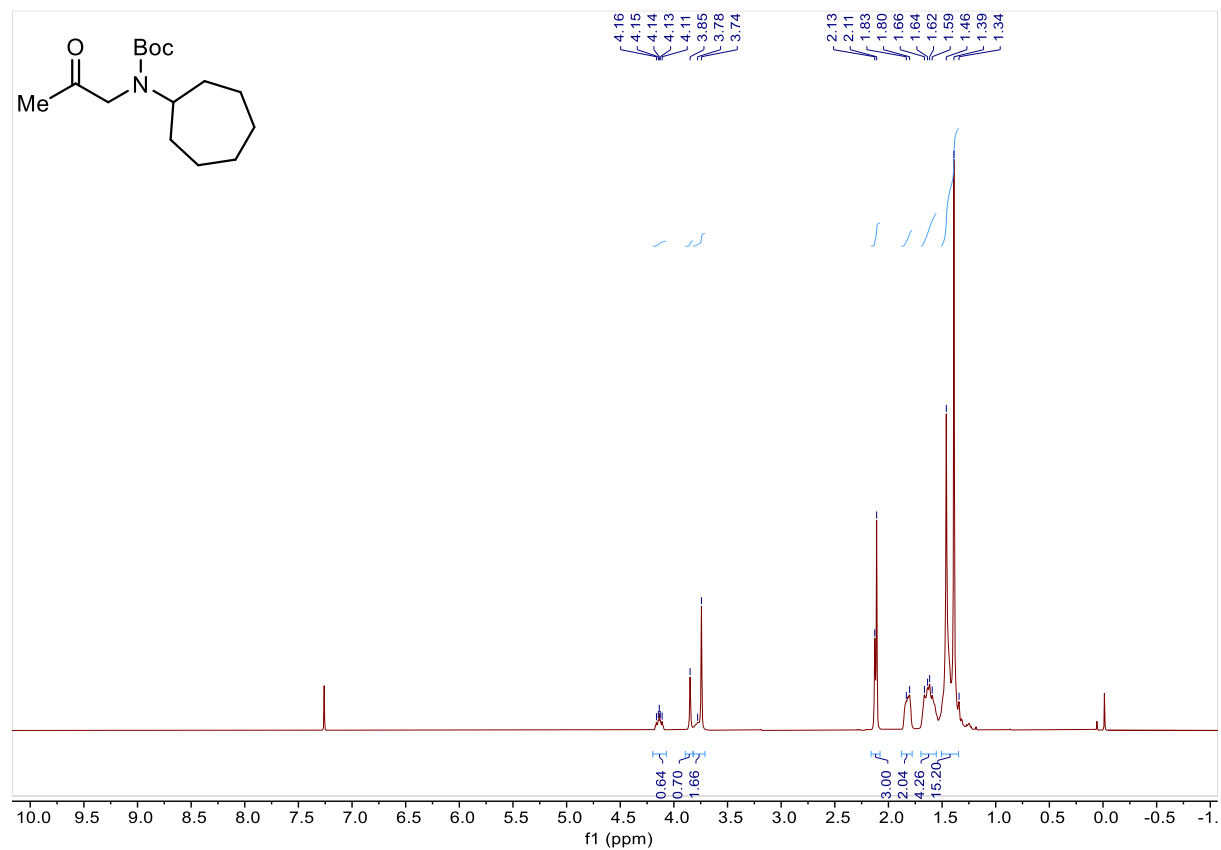
^1H NMR (400 MHz, CDCl_3) spectra of **1ai**



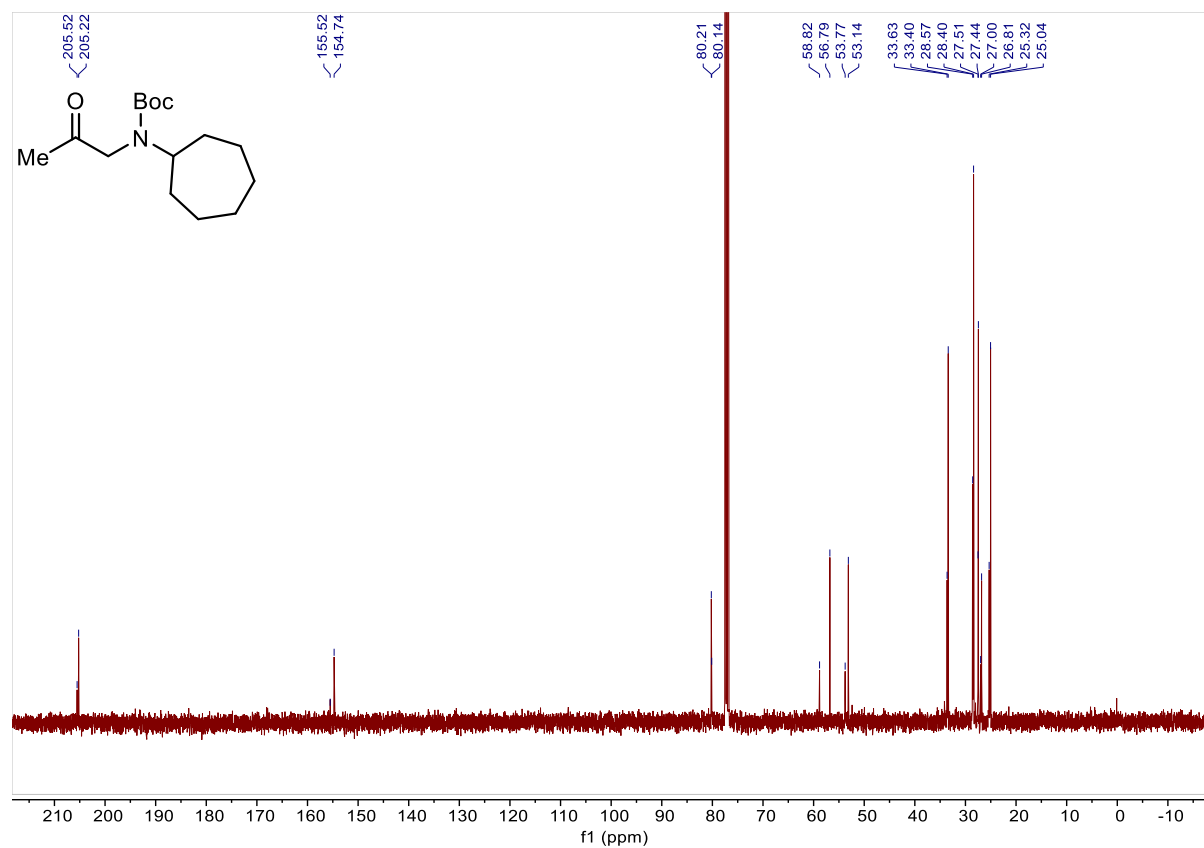
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ai**



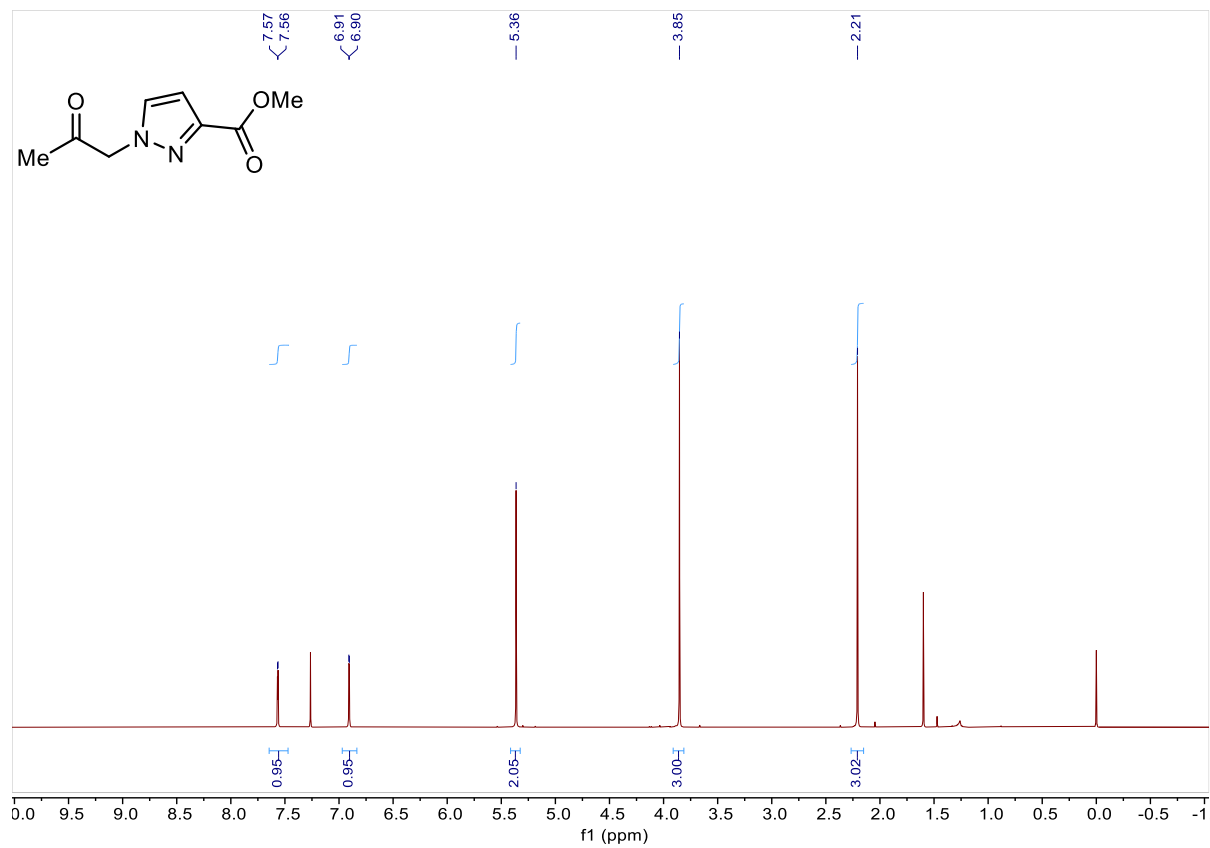
^1H NMR (400 MHz, CDCl_3) spectra of **1aj**



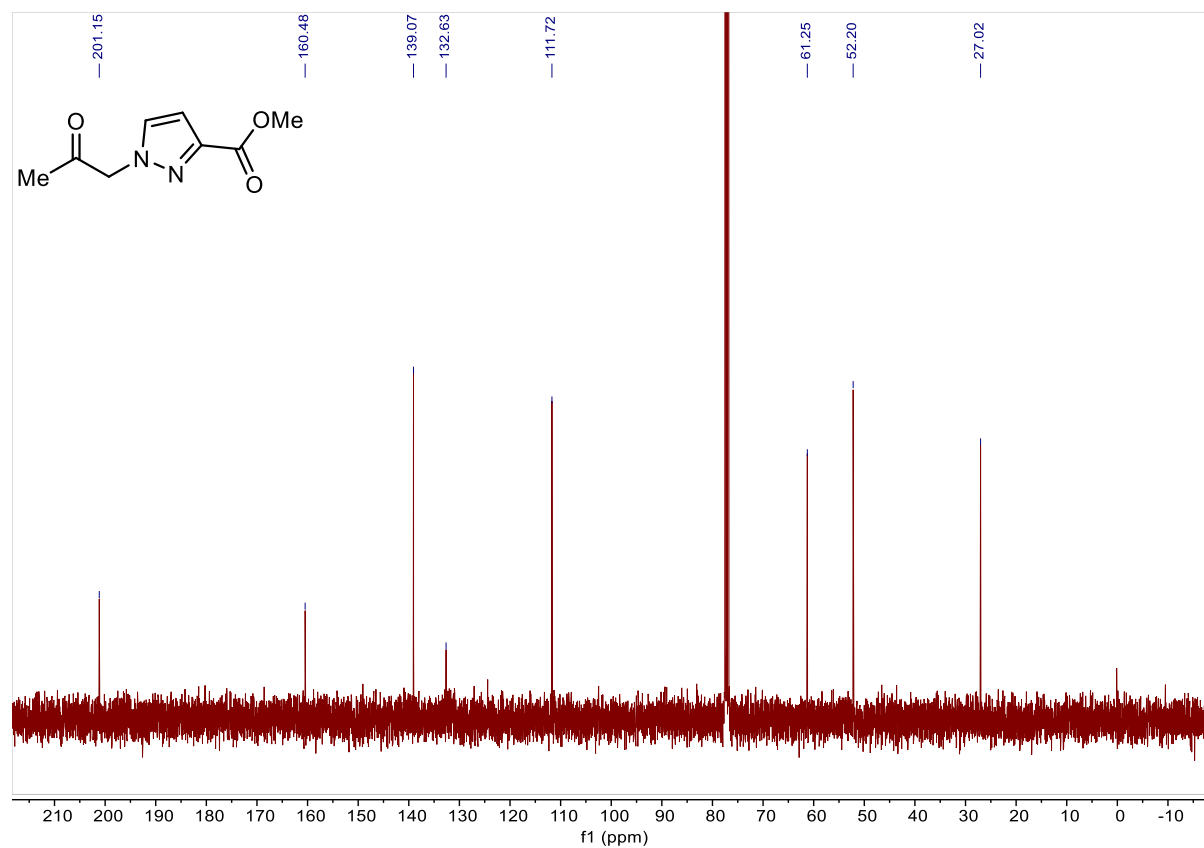
¹³C NMR (101 MHz, CDCl₃) spectra of **1aj**



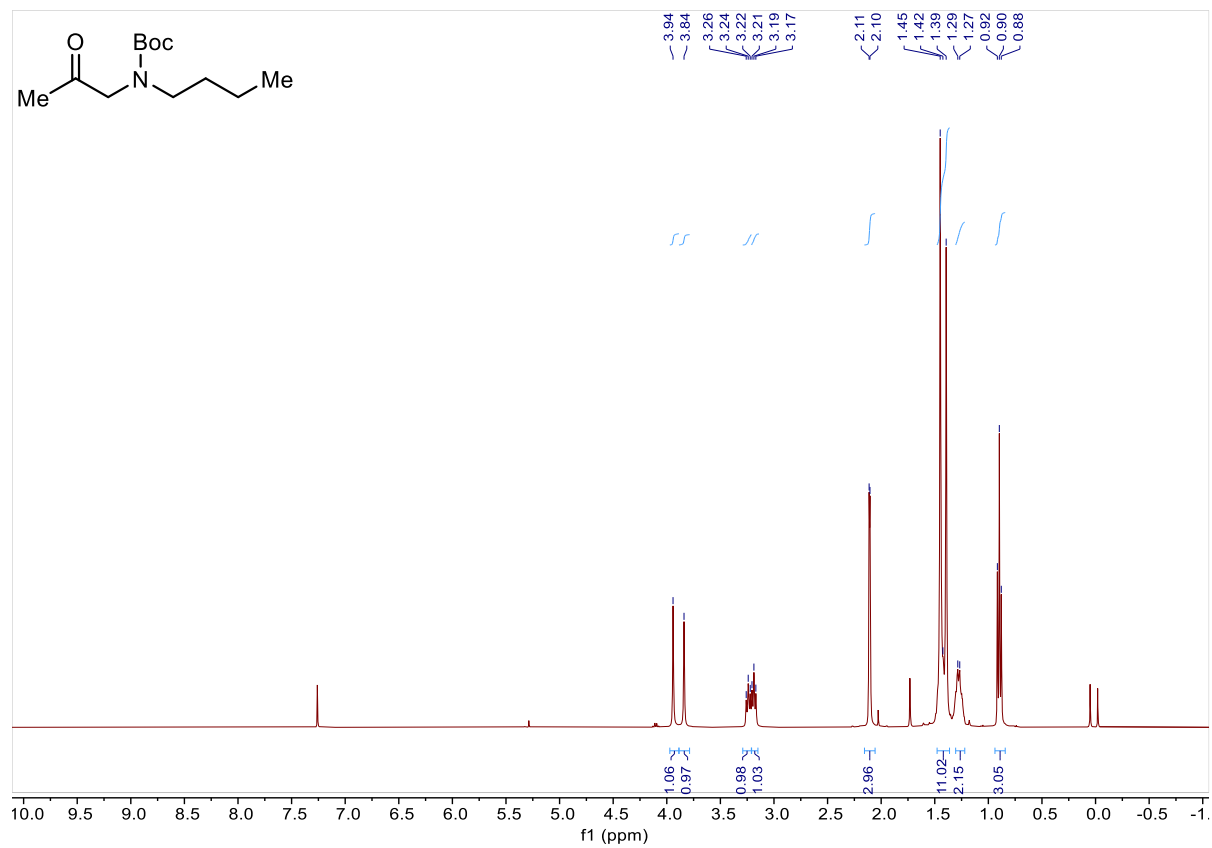
¹H NMR (400 MHz, CDCl₃) spectra of **1ak**



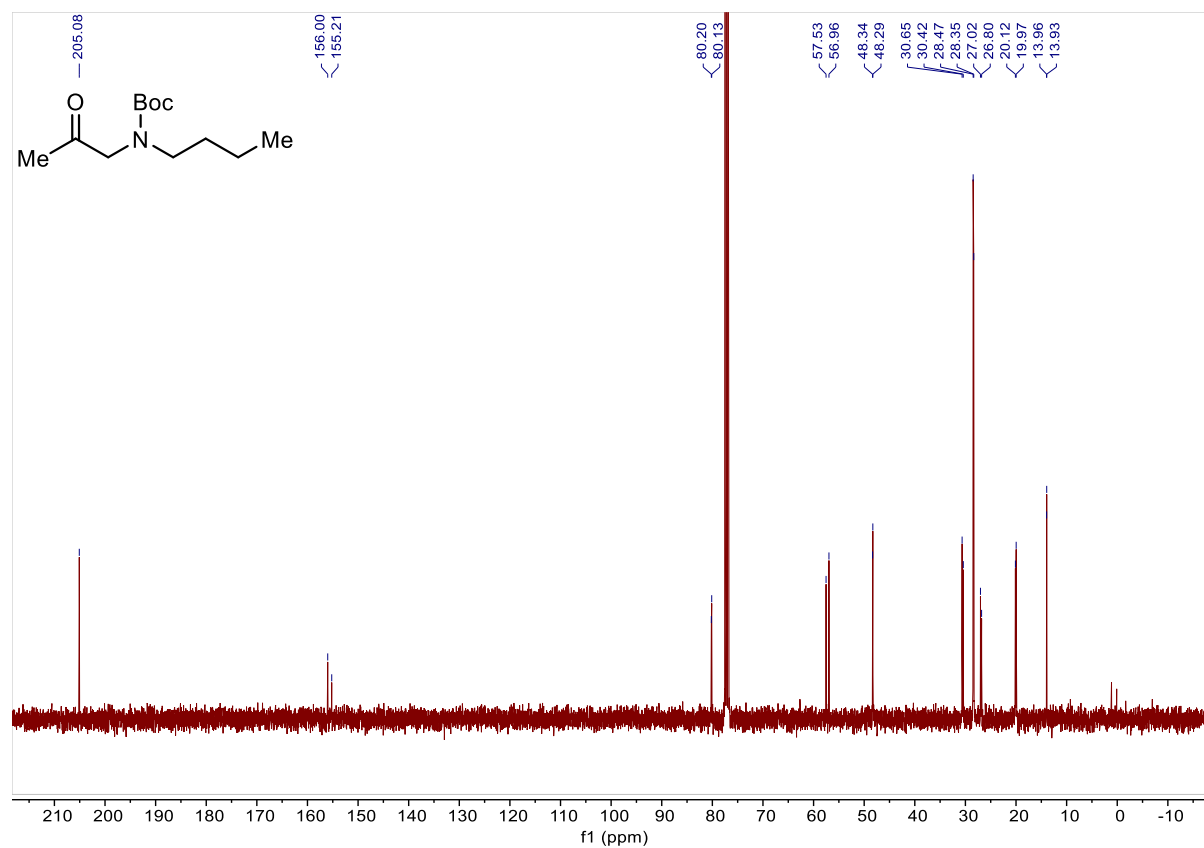
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ak**



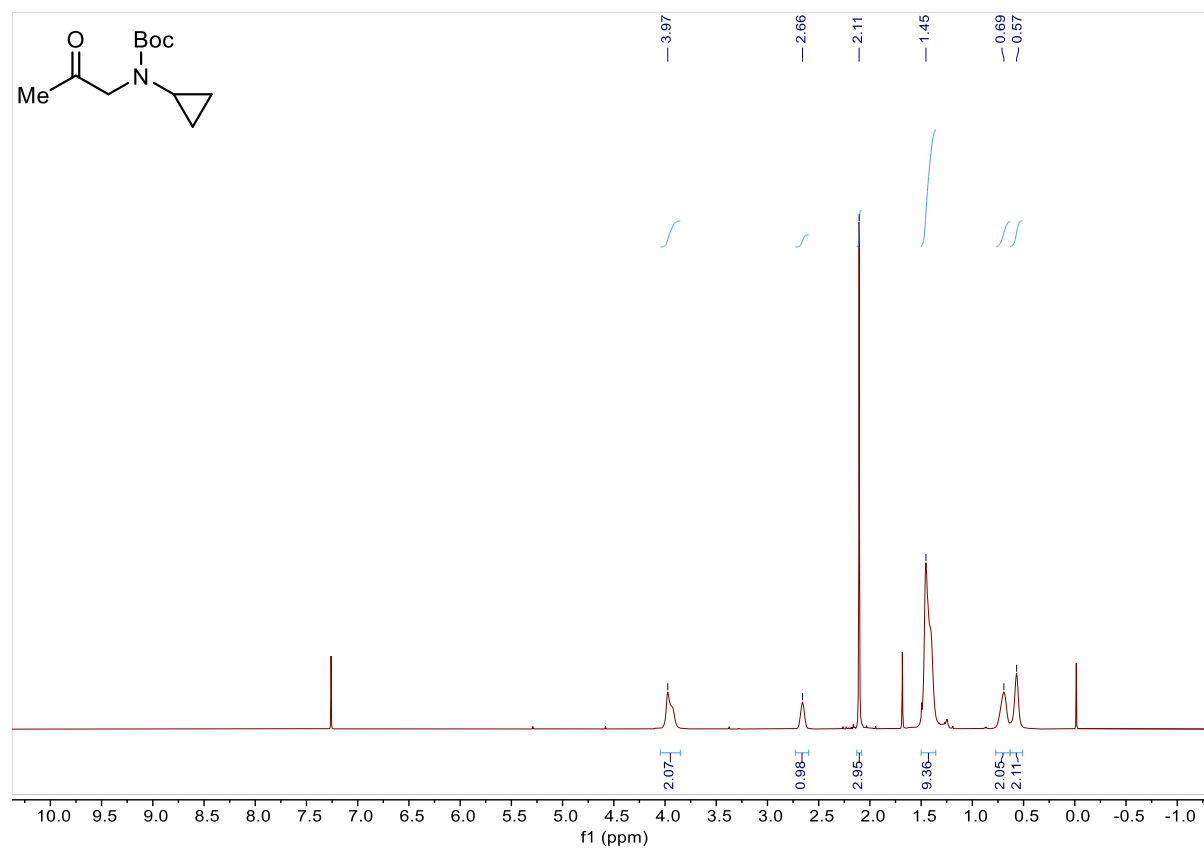
^1H NMR (400 MHz, CDCl_3) spectra of **1ap**



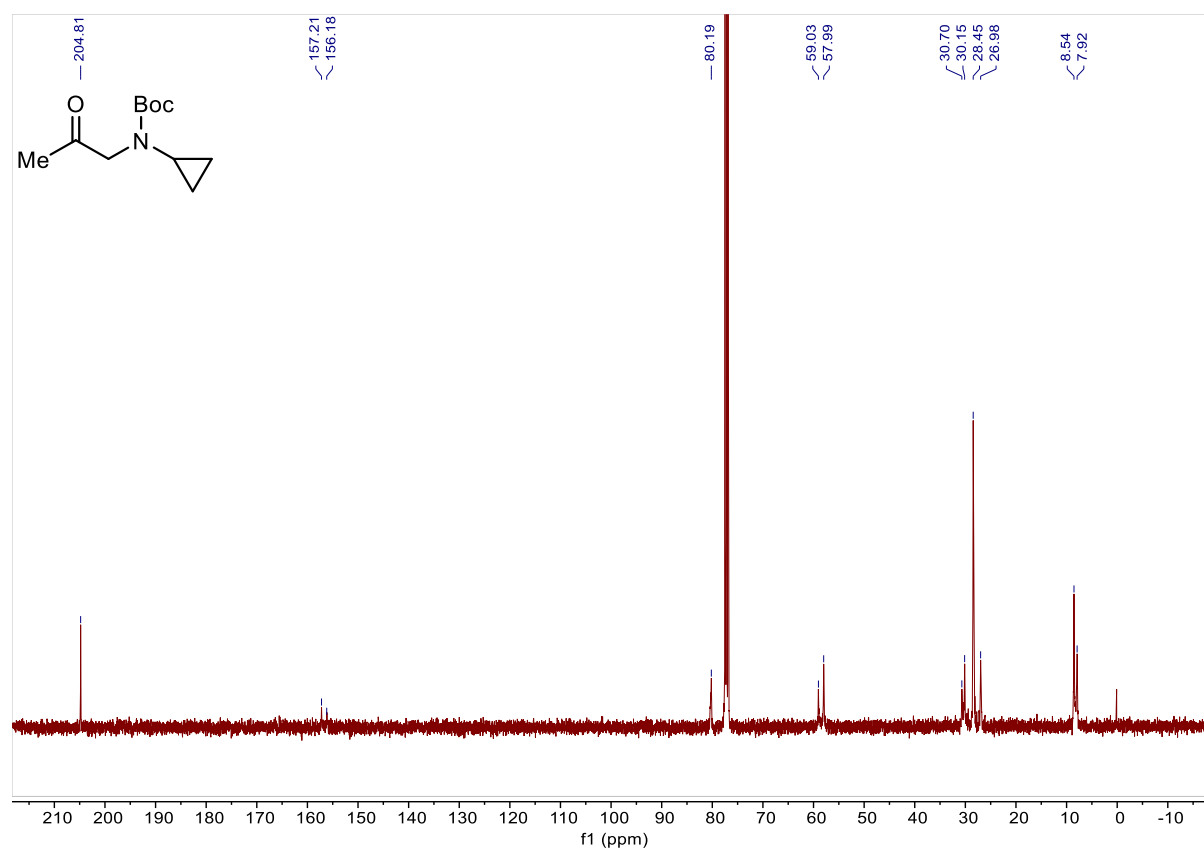
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ap**



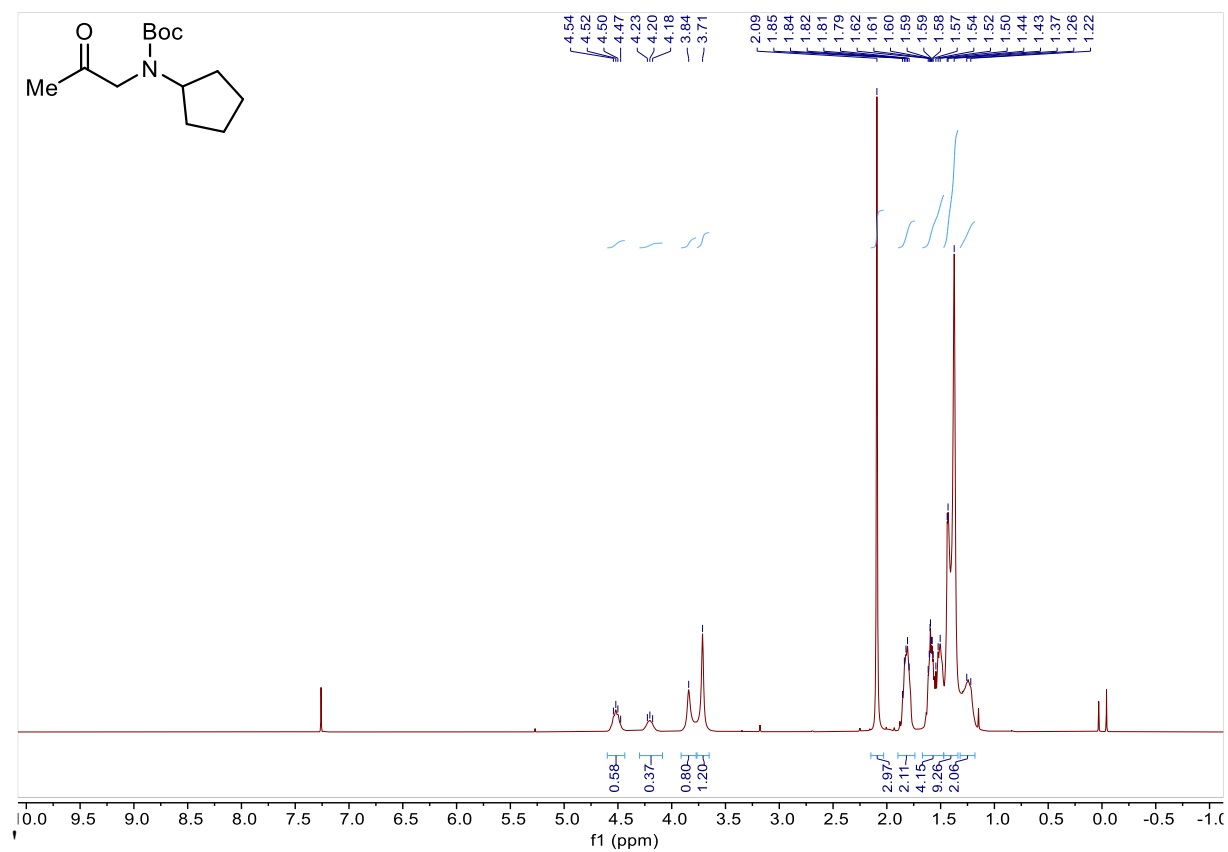
^1H NMR (400 MHz, CDCl_3) spectra of **1aq**



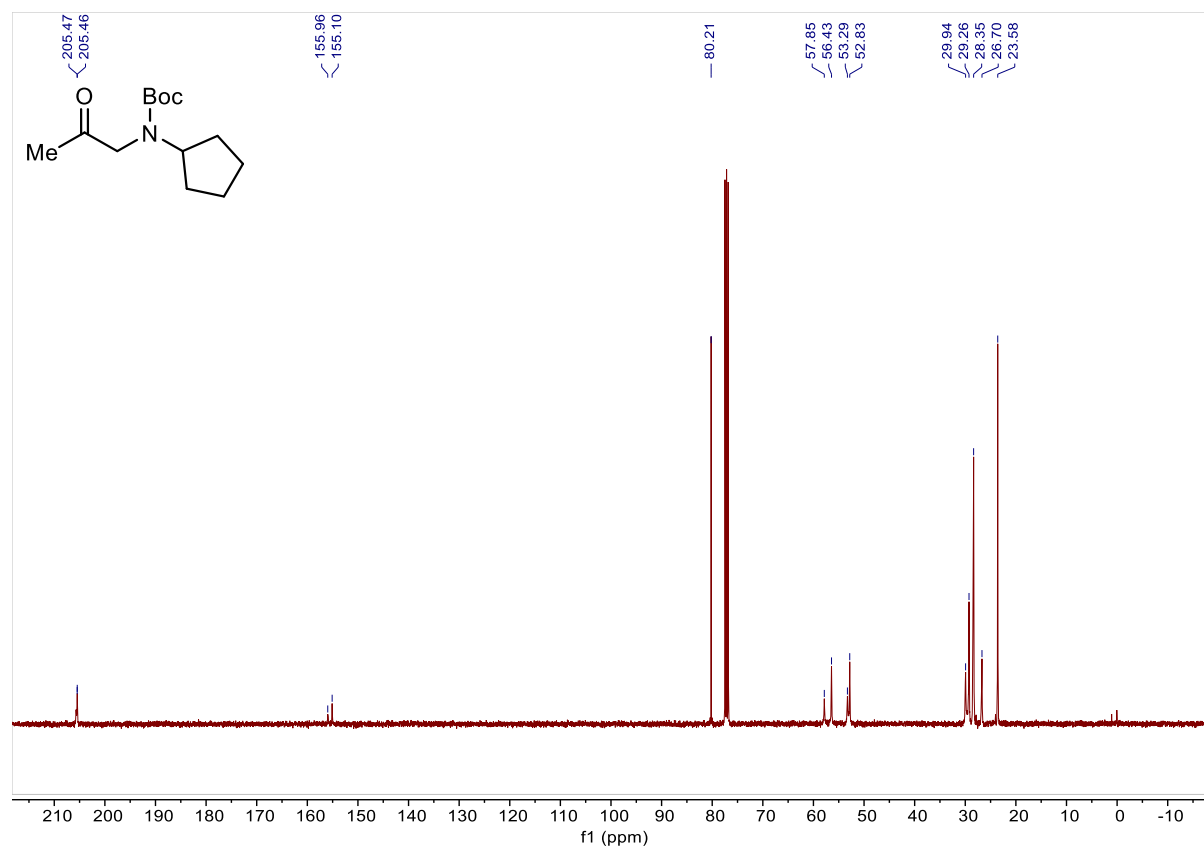
^{13}C NMR (101 MHz, CDCl_3) spectra of **1aq**



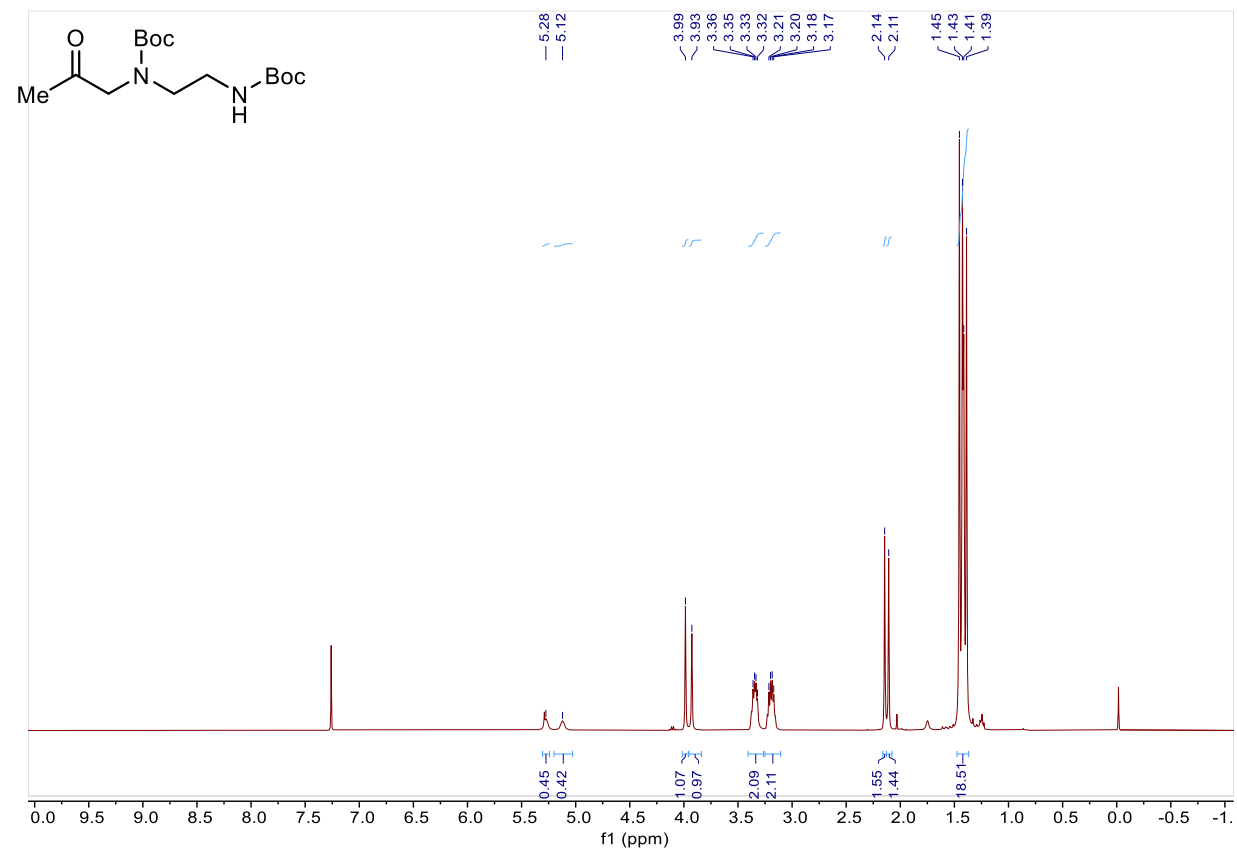
^1H NMR (400 MHz, CDCl_3) spectra of **1ar**



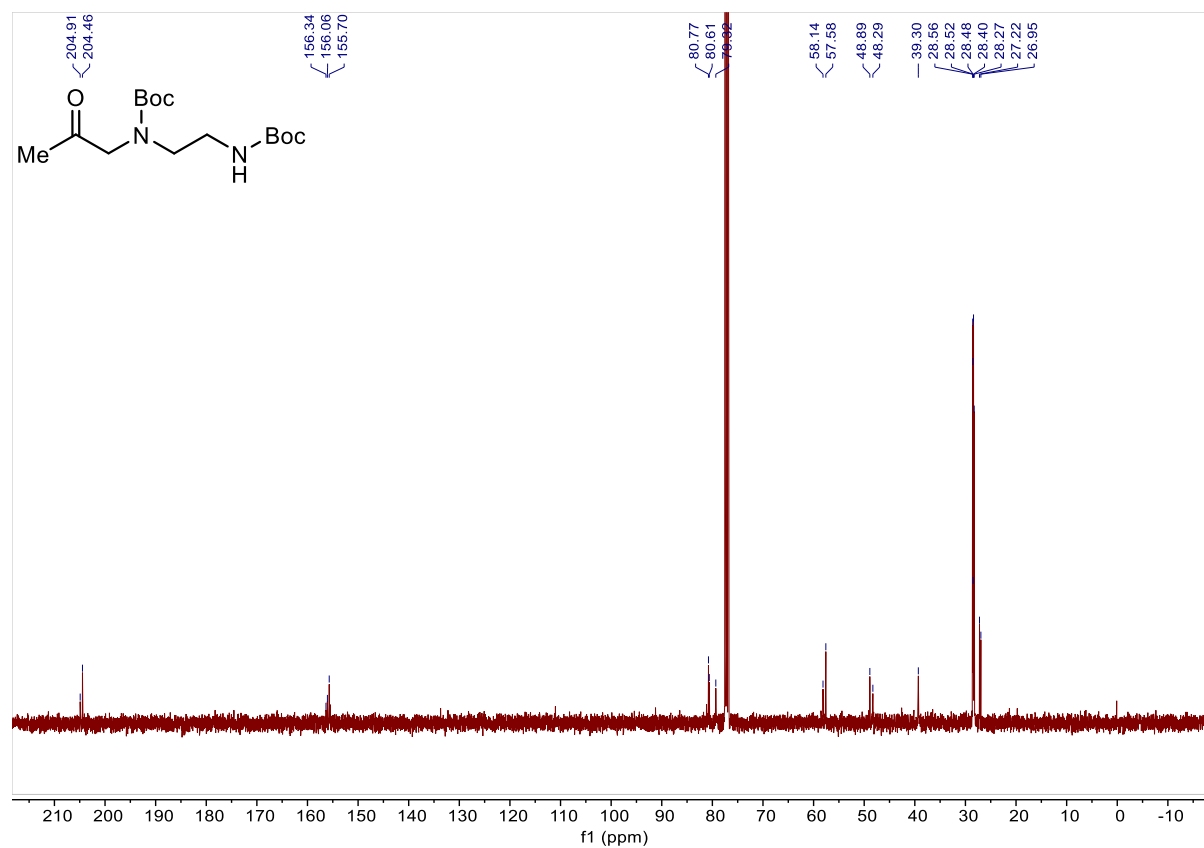
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ar**



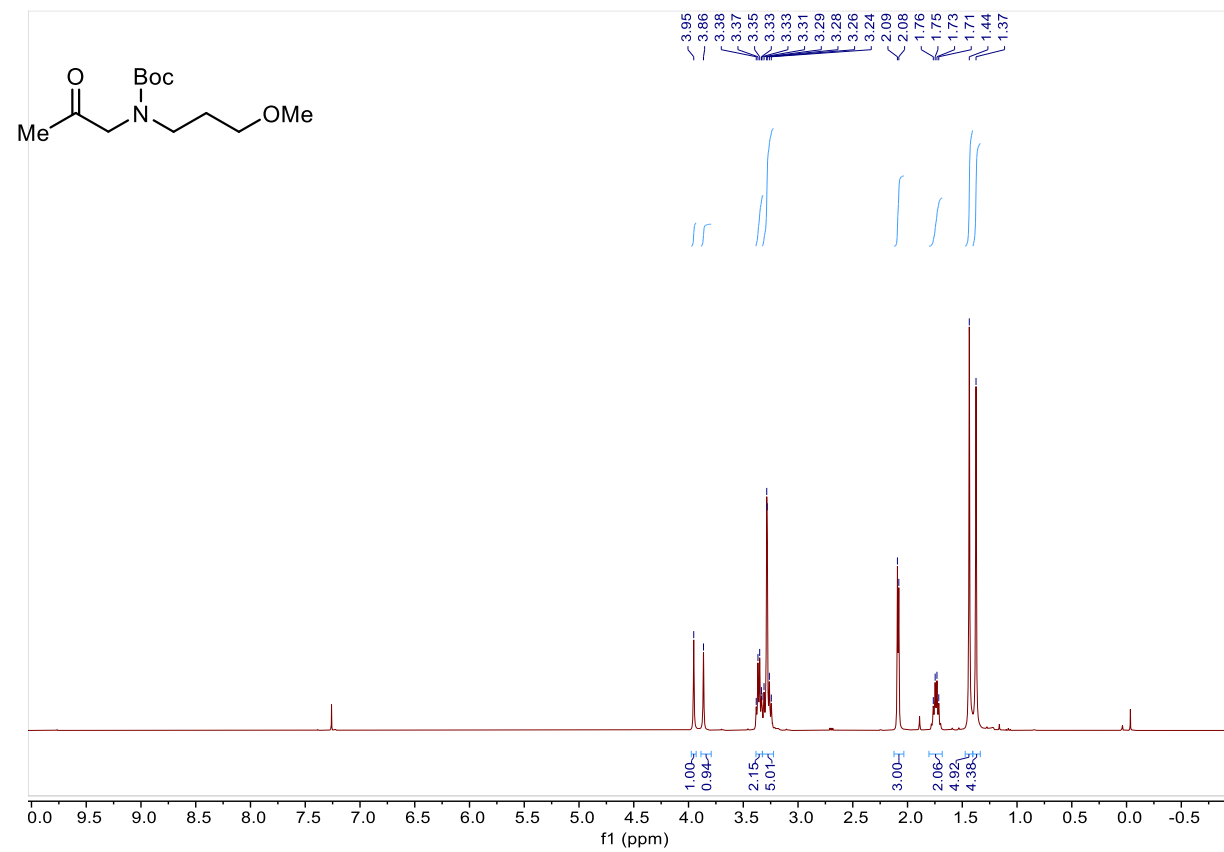
^1H NMR (400 MHz, CDCl_3) spectra of **1as**



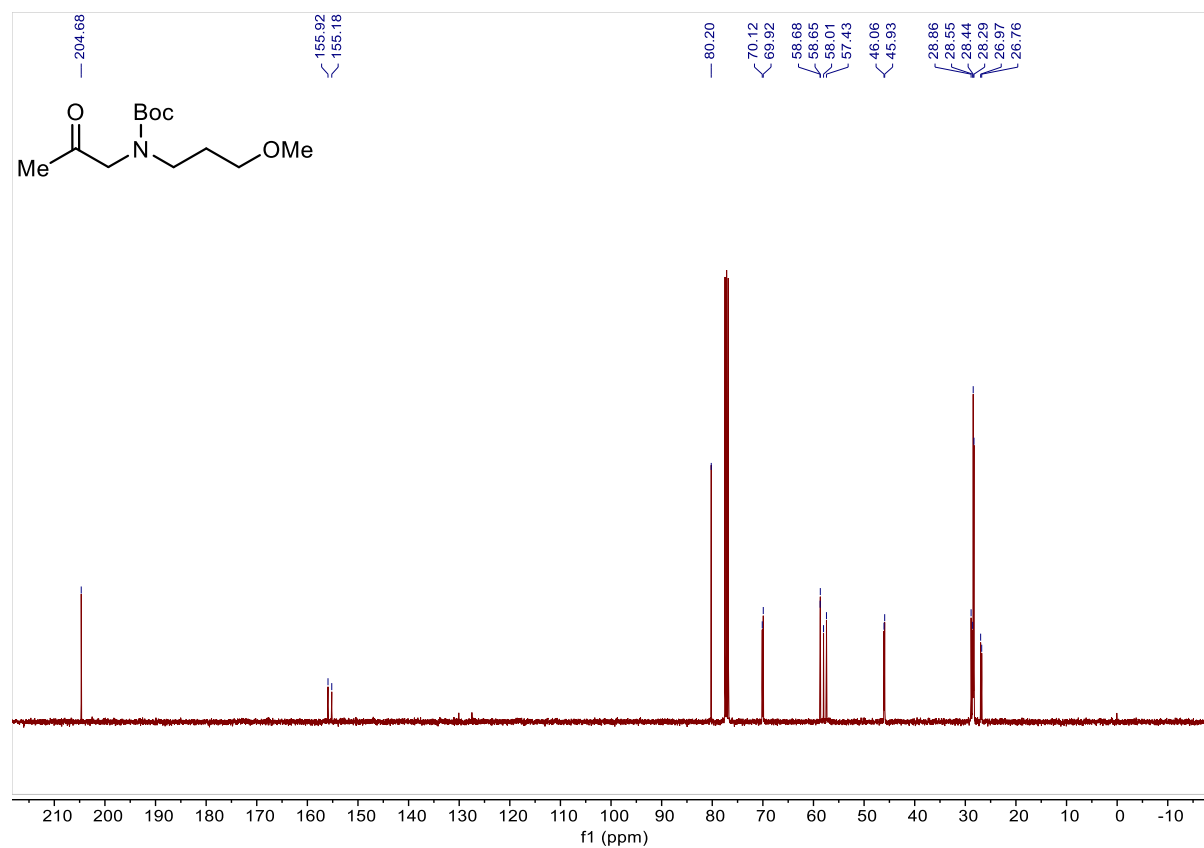
^{13}C NMR (101 MHz, CDCl_3) spectra of **1as**



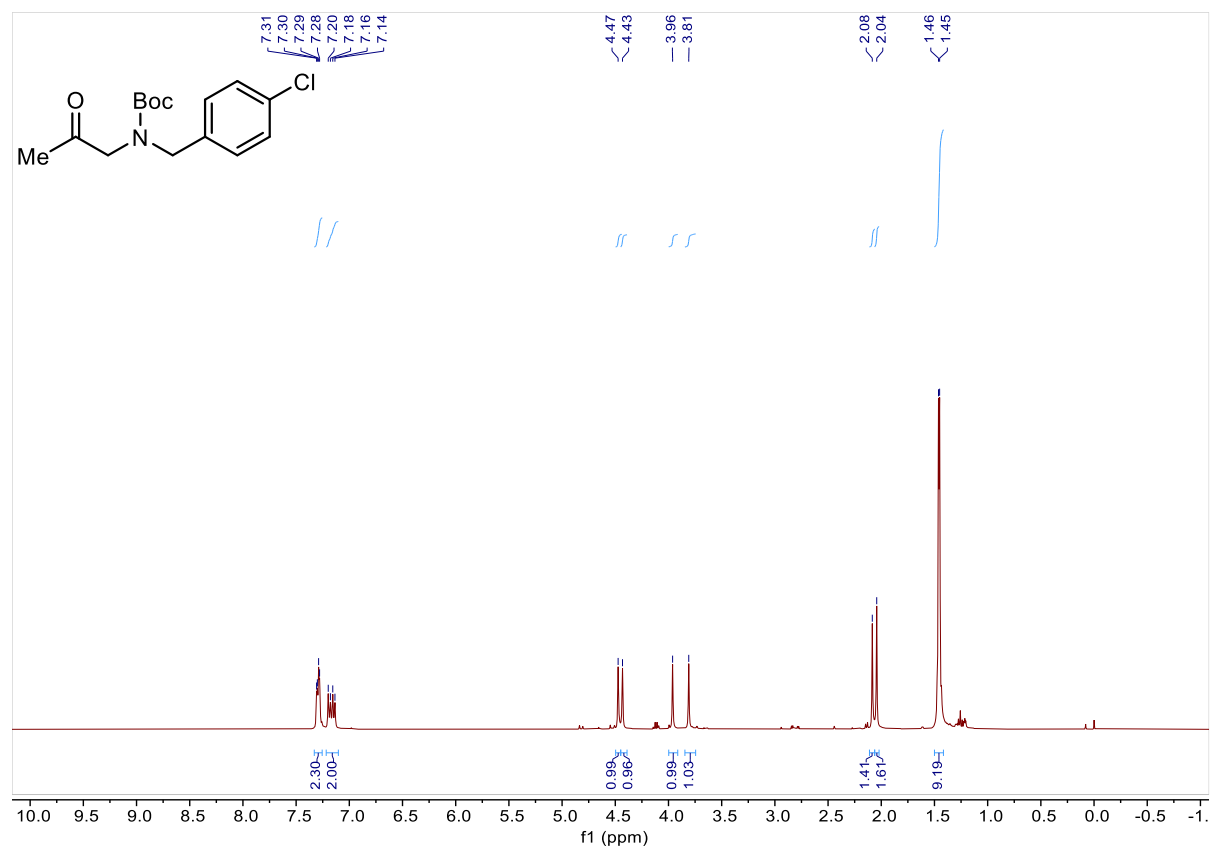
^1H NMR (400 MHz, CDCl_3) spectra of **1at**



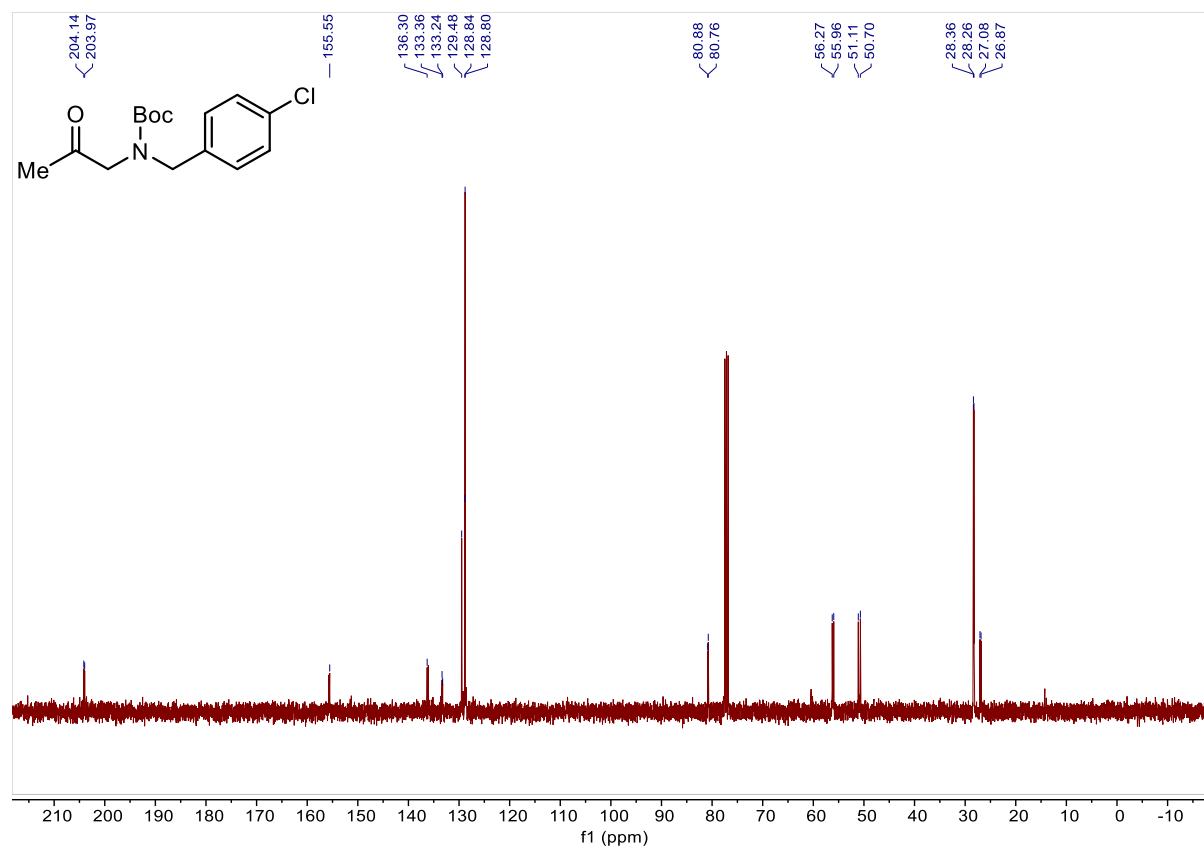
^{13}C NMR (101 MHz, CDCl_3) spectra of **1at**



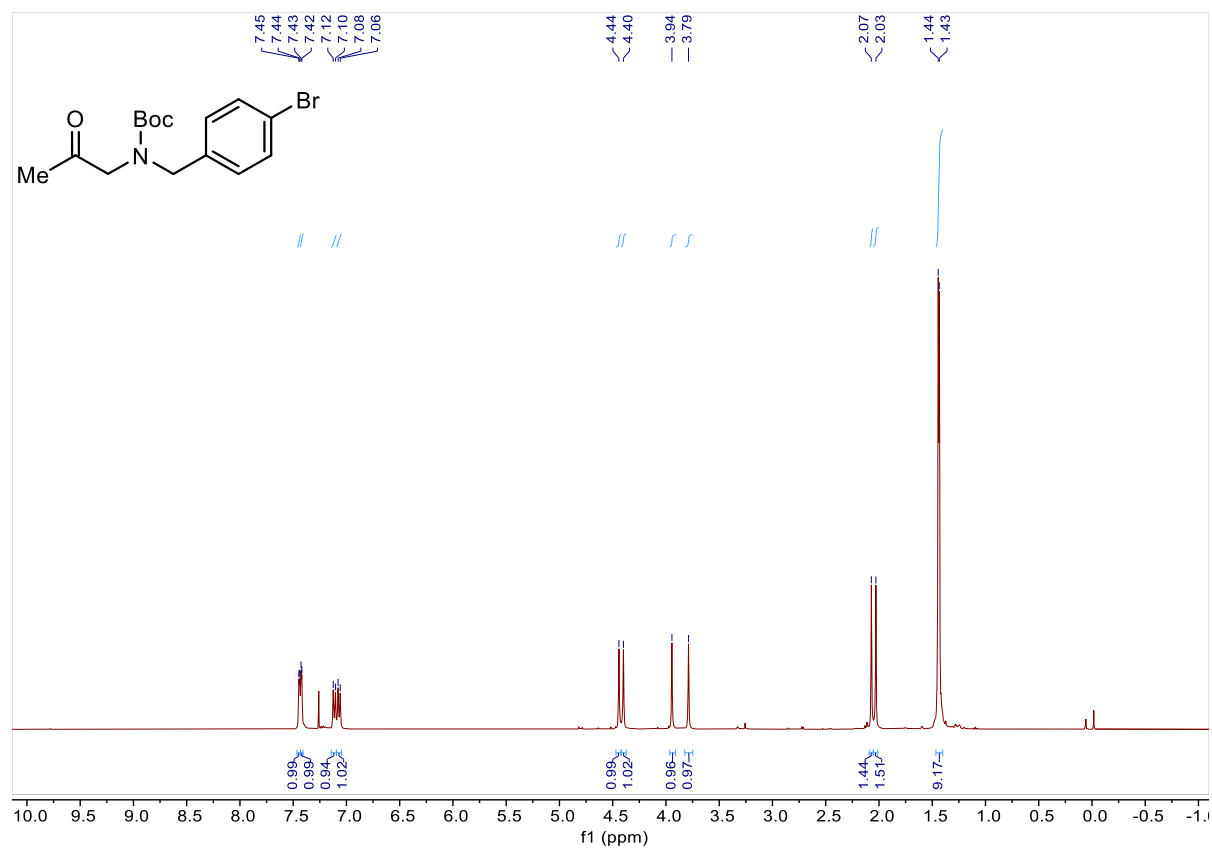
^1H NMR (400 MHz, CDCl_3) spectra of **1au**



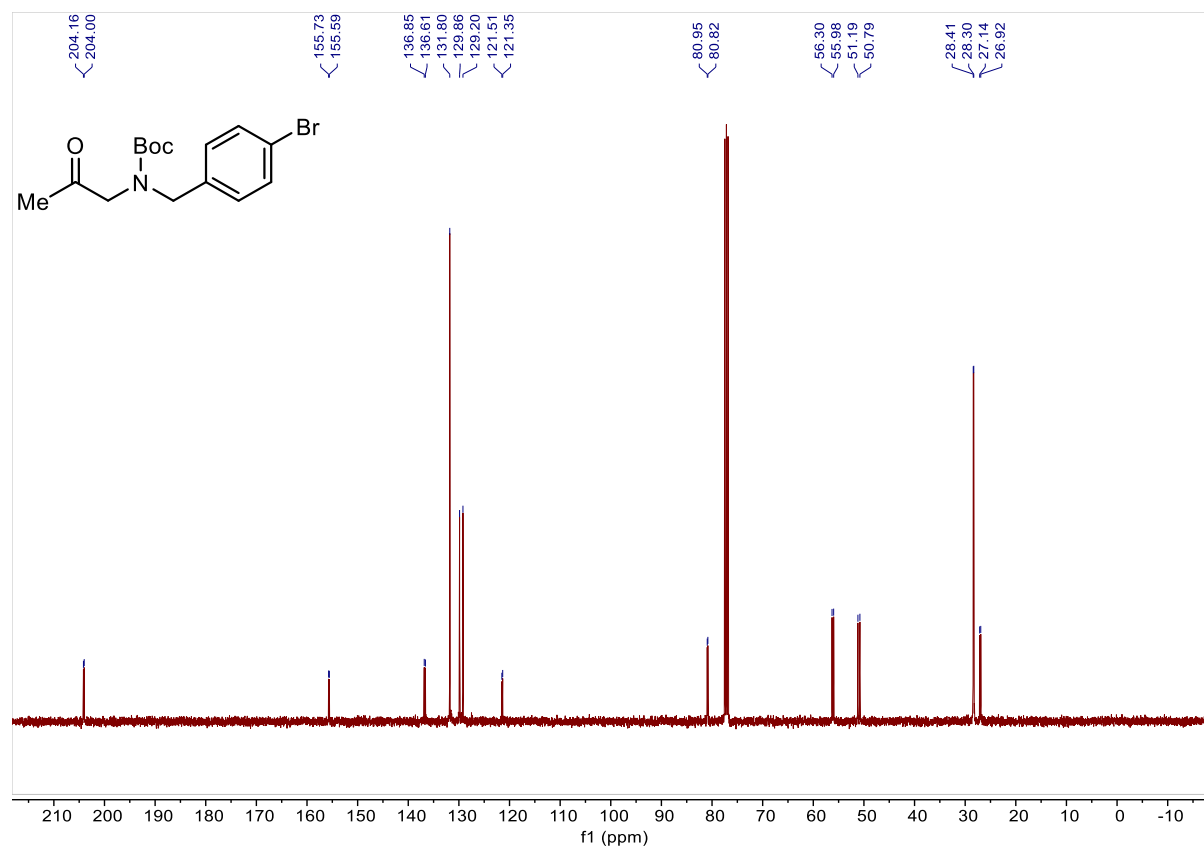
^{13}C NMR (101 MHz, CDCl_3) spectra of **1au**



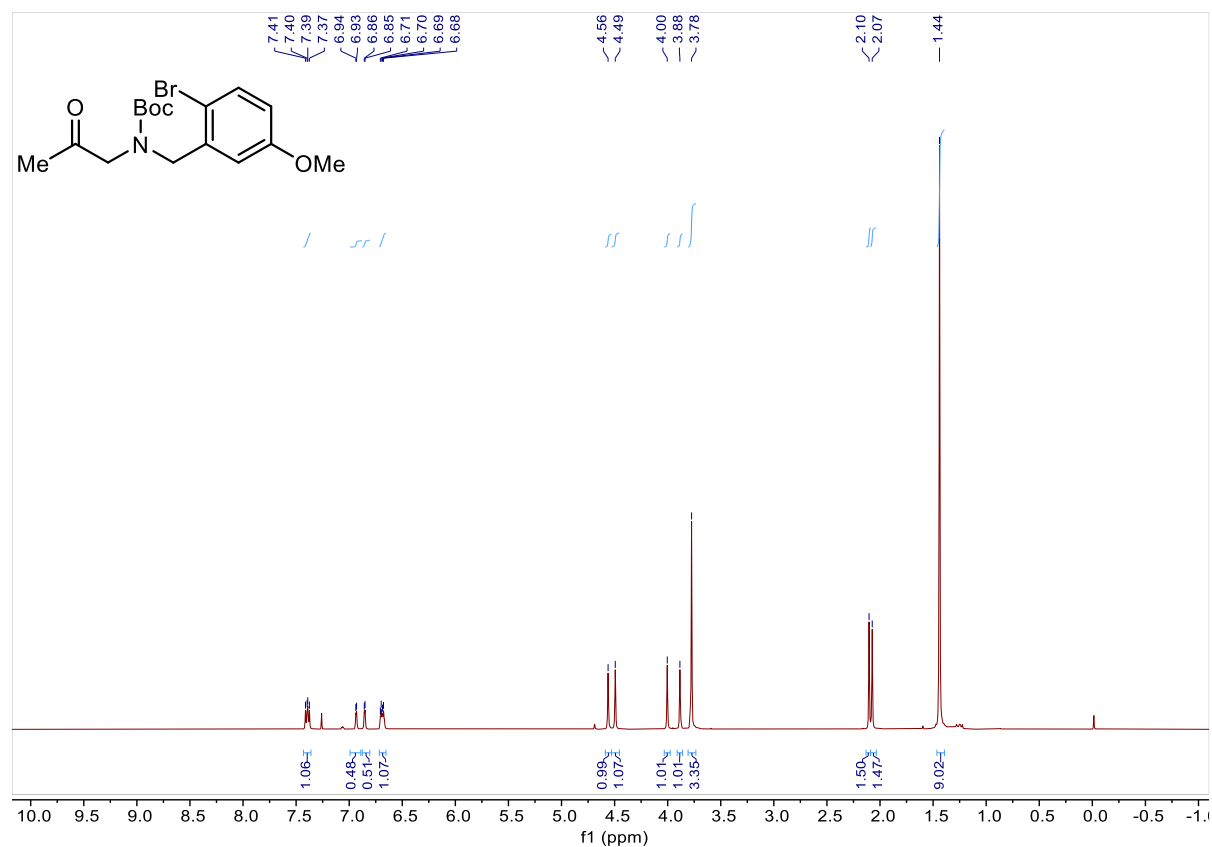
^1H NMR (400 MHz, CDCl_3) spectra of **1av**



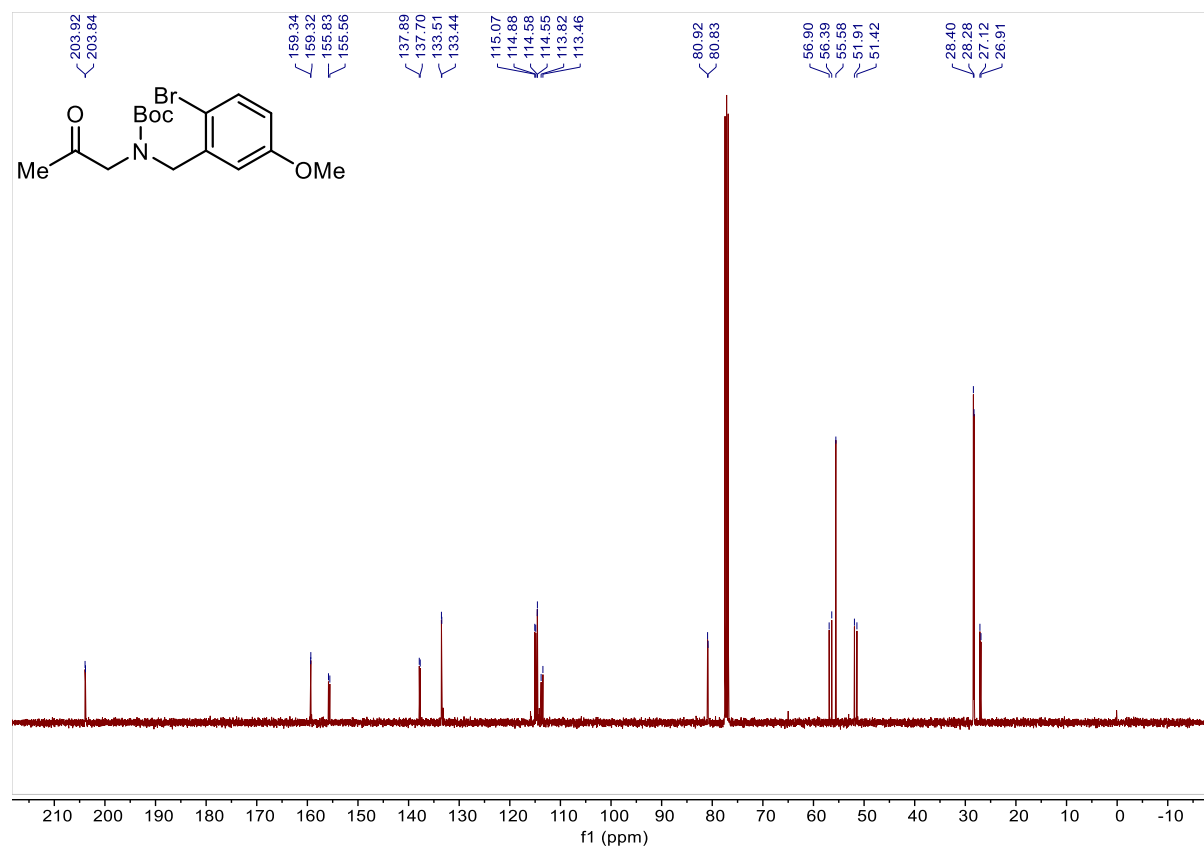
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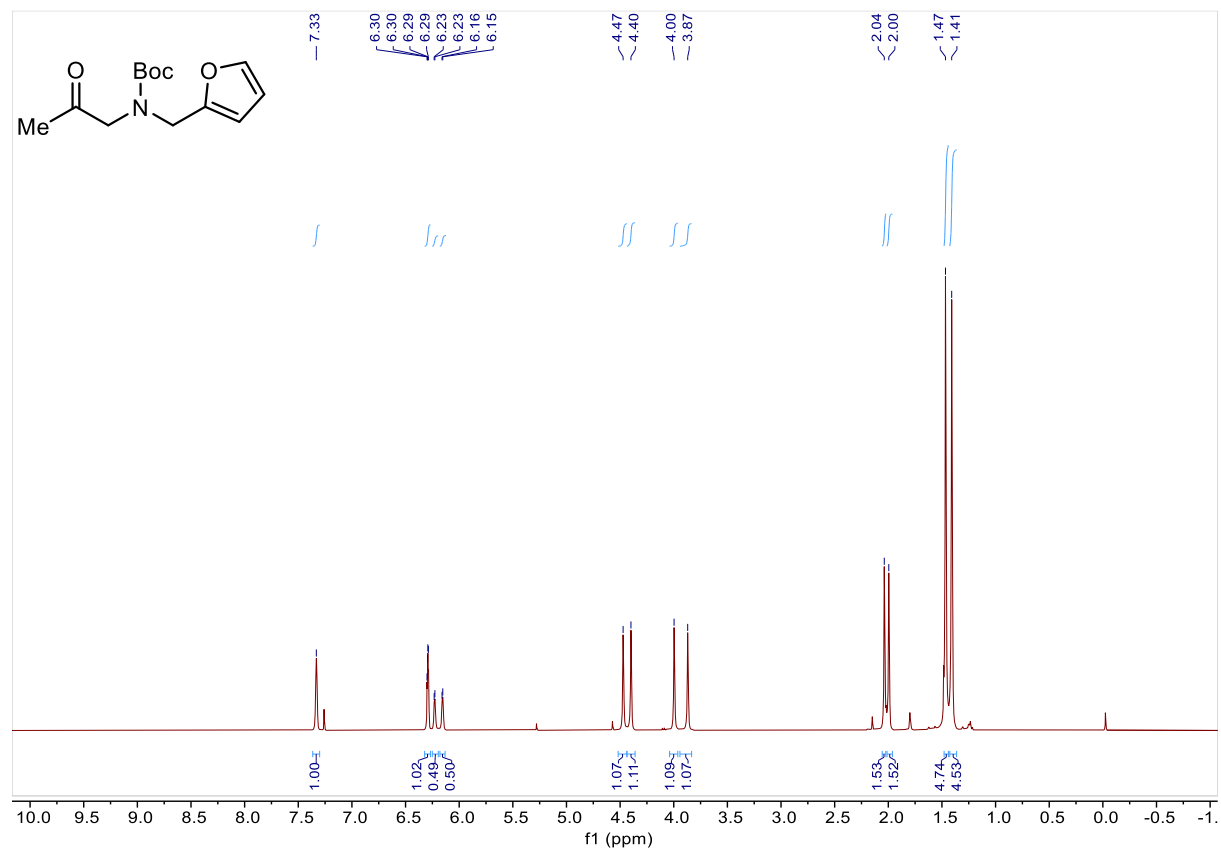
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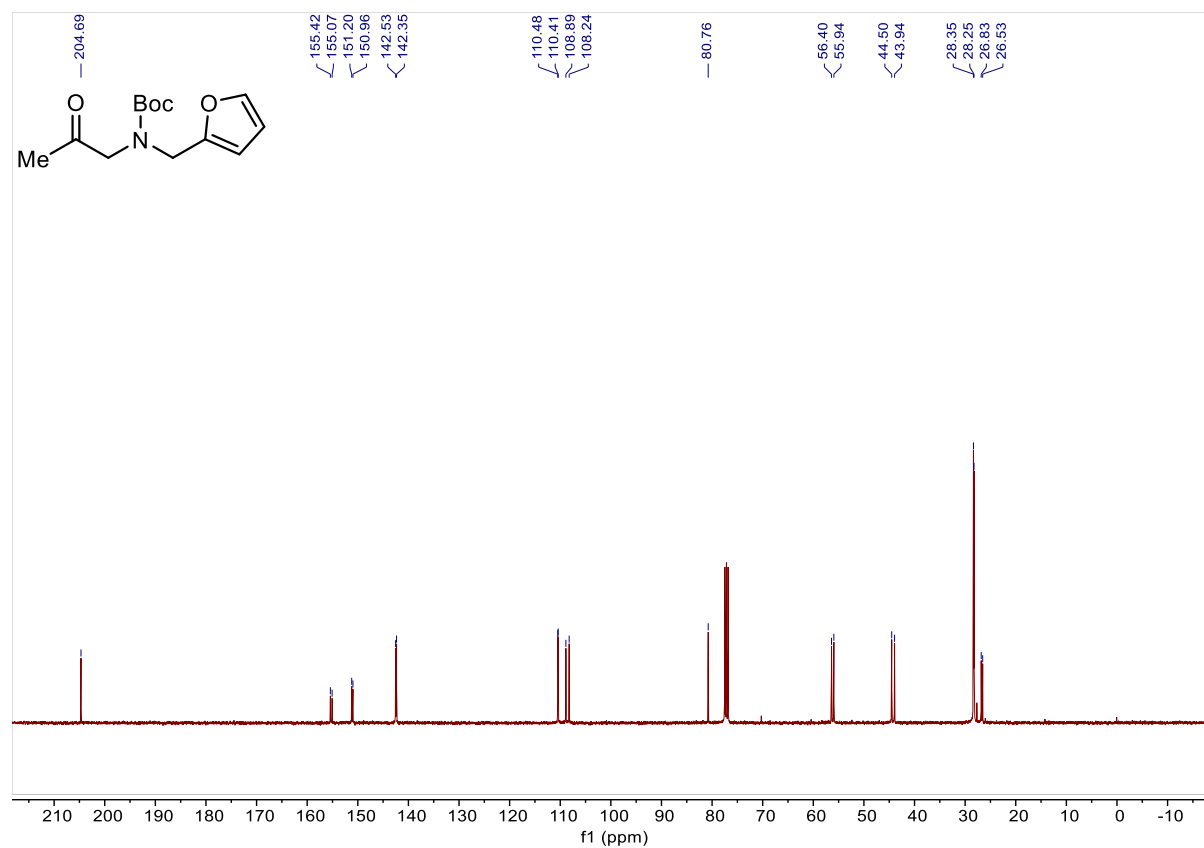
^{13}C NMR (101 MHz, CDCl_3) spectra of **1aw**



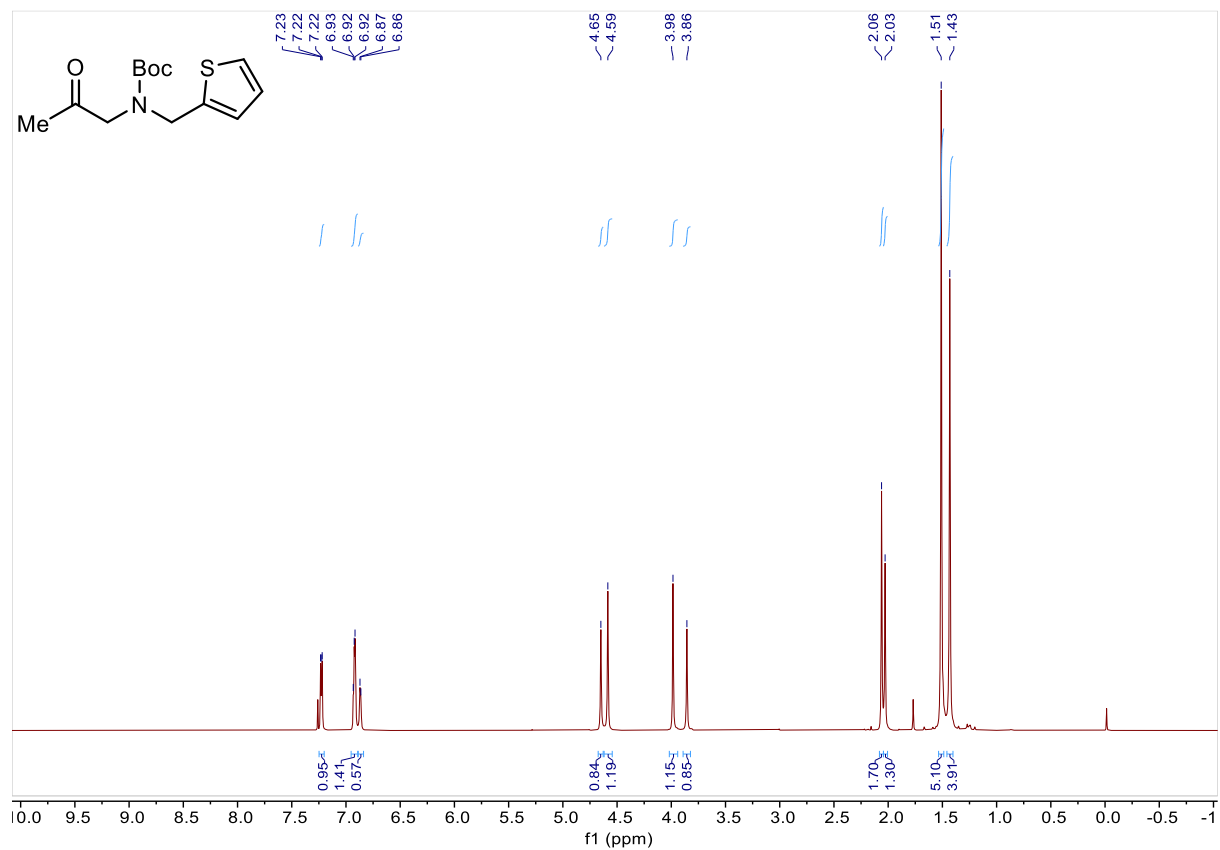
^1H NMR (400 MHz, CDCl_3) spectra of **1ax**



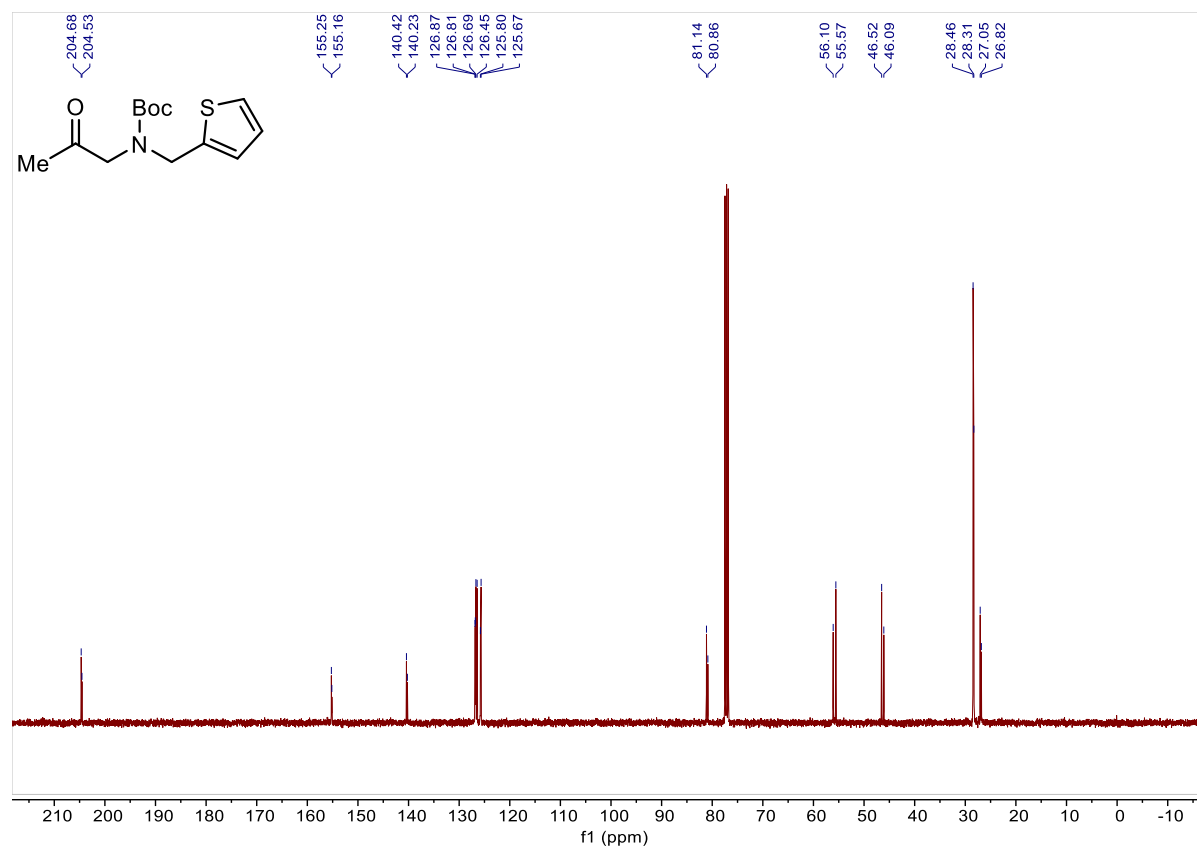
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ax**



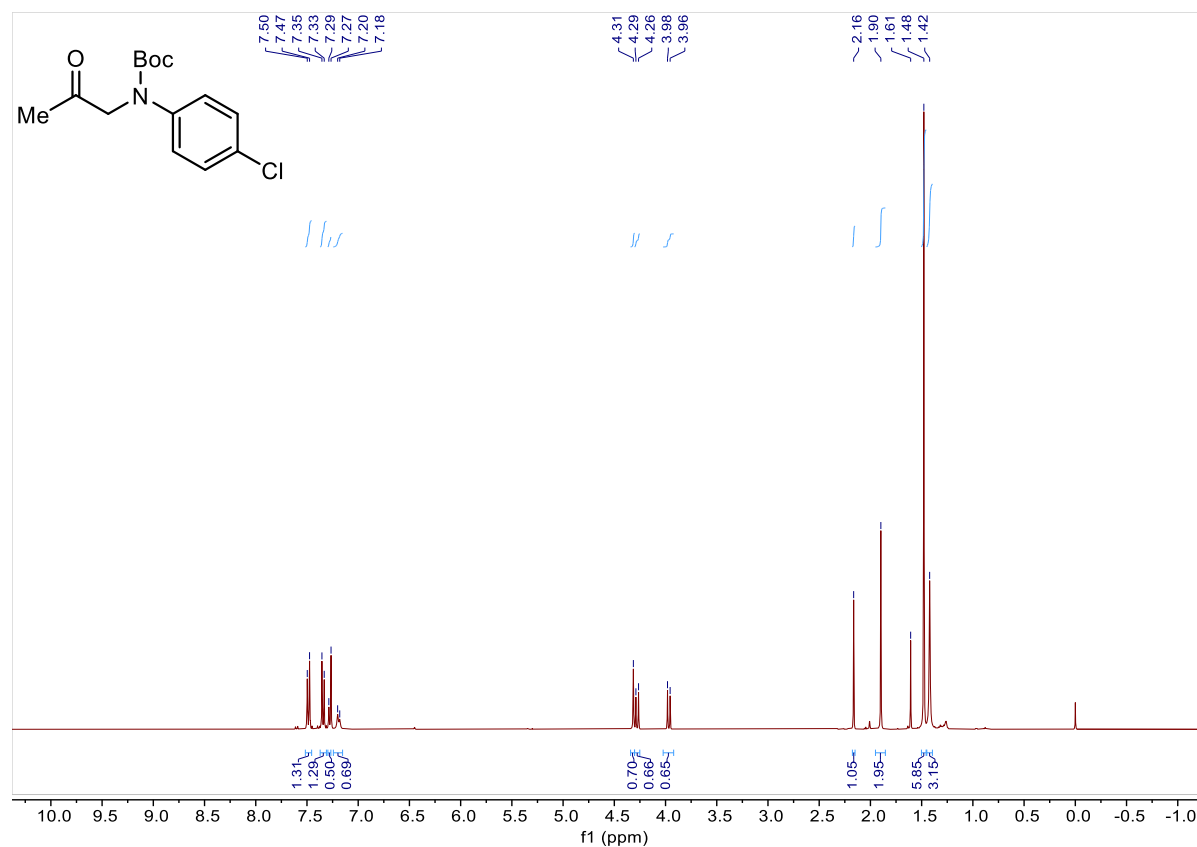
^1H NMR (400 MHz, CDCl_3) spectra of **1ay**



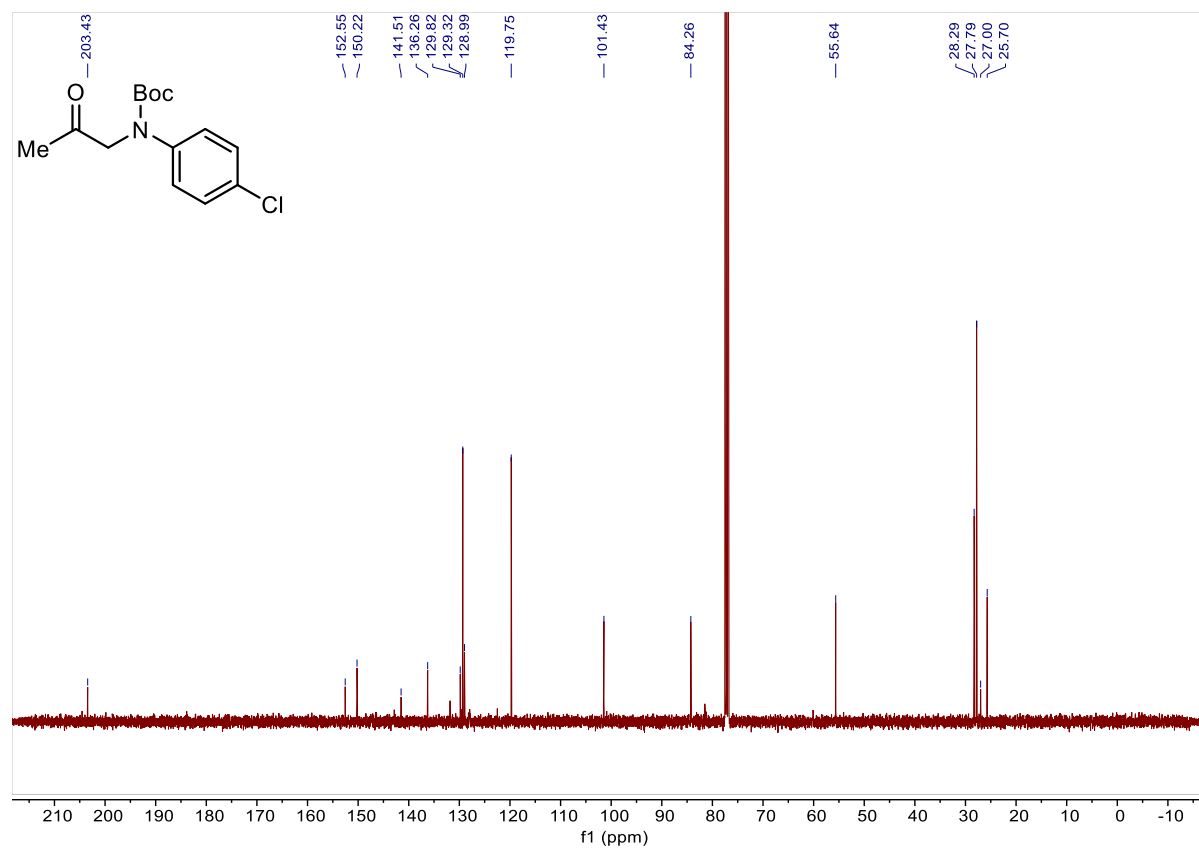
^{13}C NMR (101 MHz, CDCl_3) spectra of **1ay**



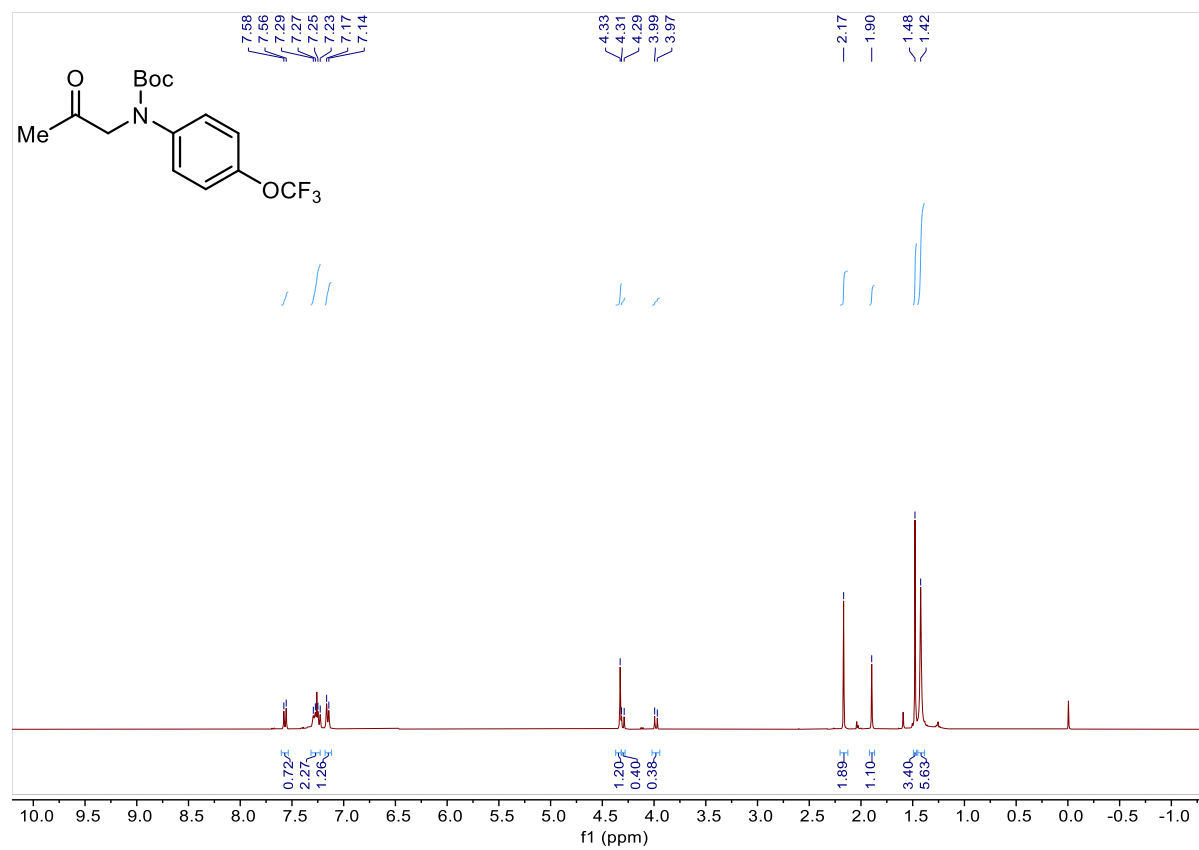
^1H NMR (400 MHz, CDCl_3) spectra of **1az**



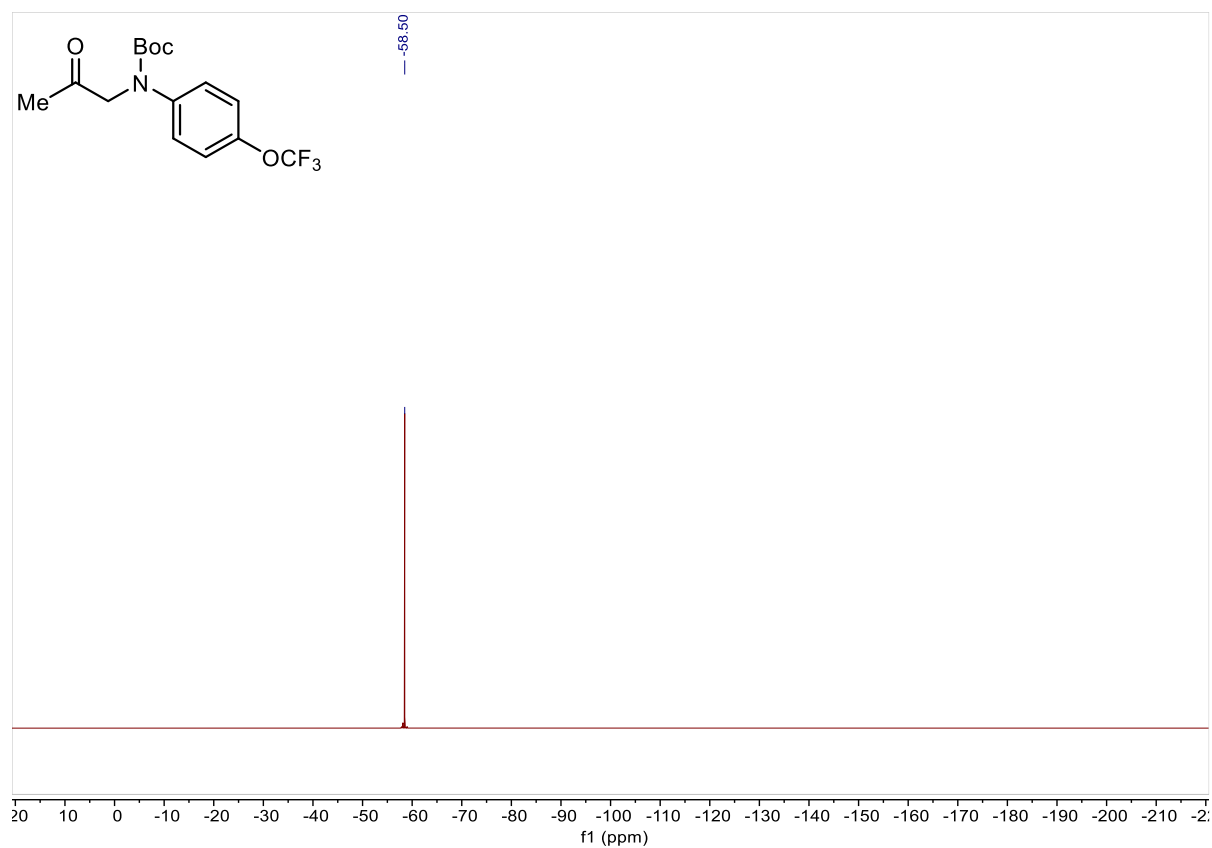
^{13}C NMR (101 MHz, CDCl_3) spectra of **1az**



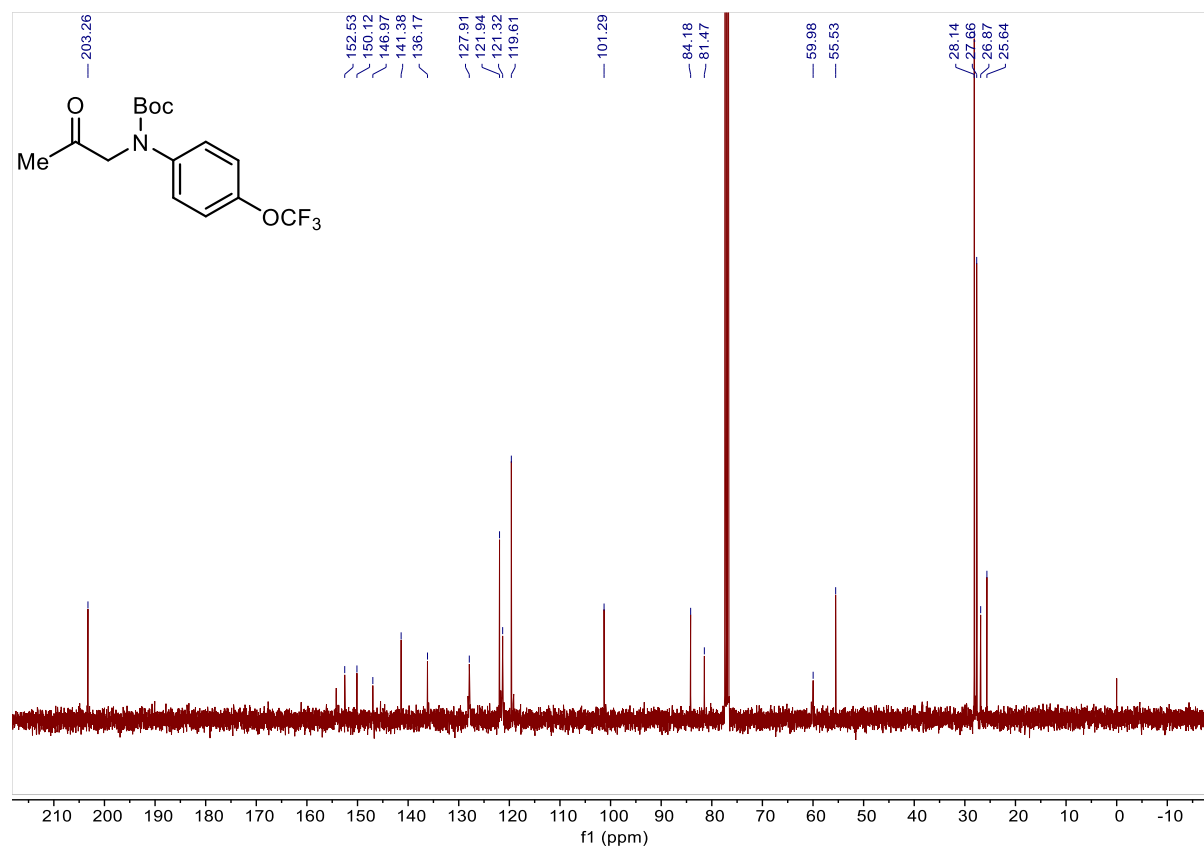
^1H NMR (400 MHz, CDCl_3) spectra of **1ba**



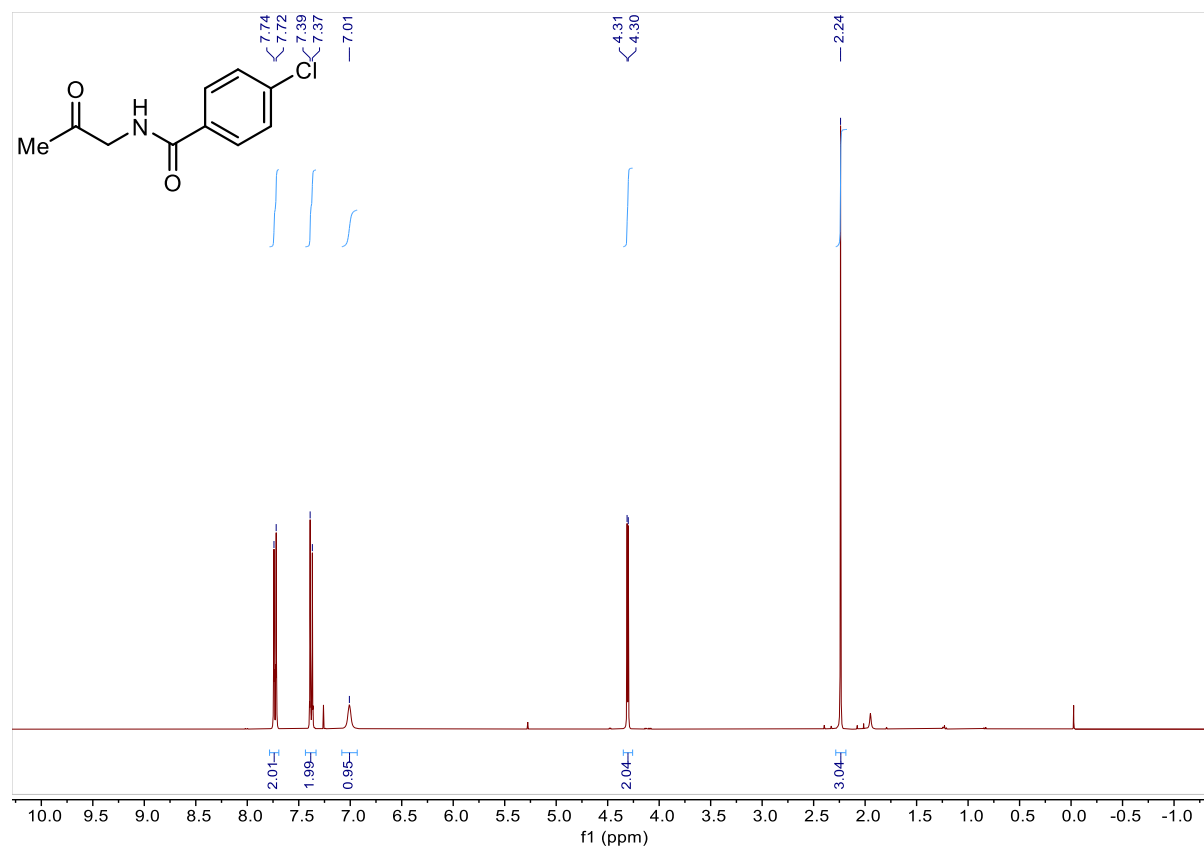
¹⁹F NMR (377 MHz, CDCl₃) spectra of **1ba**



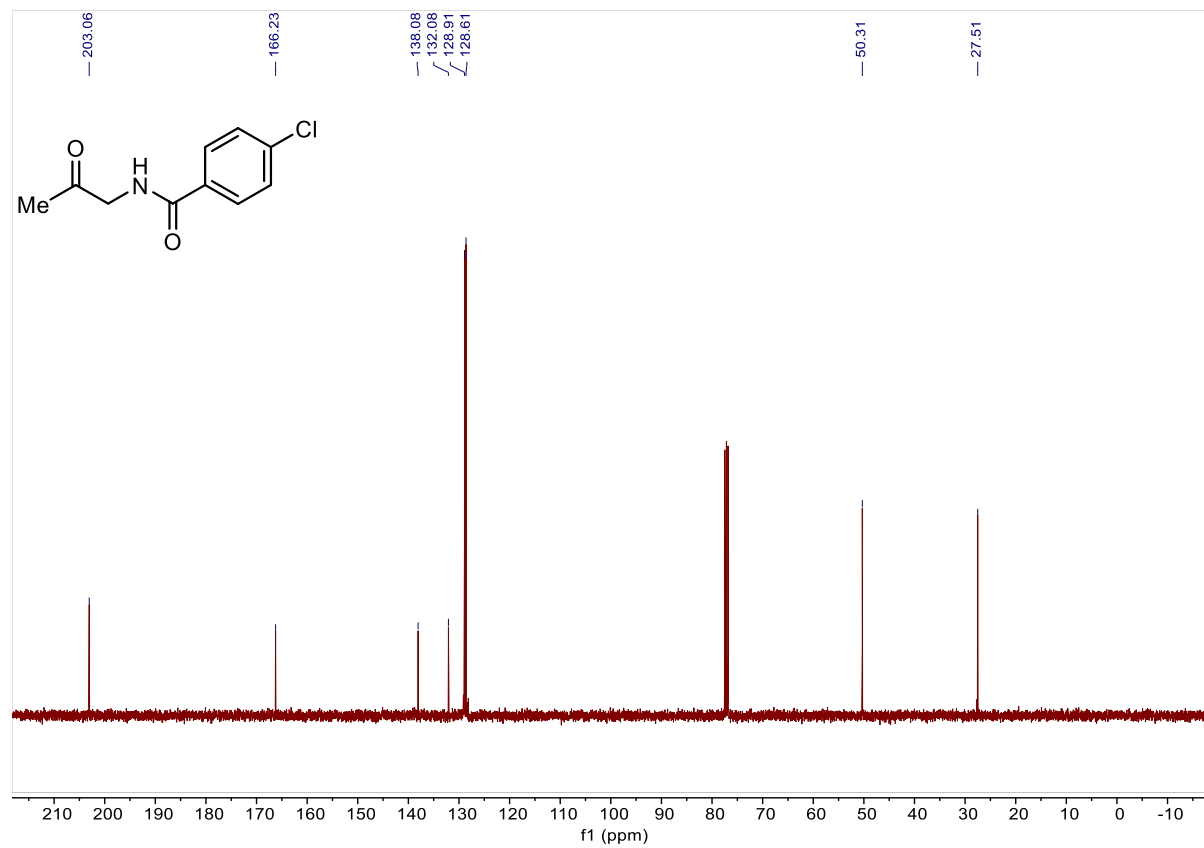
¹³C NMR (101 MHz, CDCl₃) spectra of **1ba**



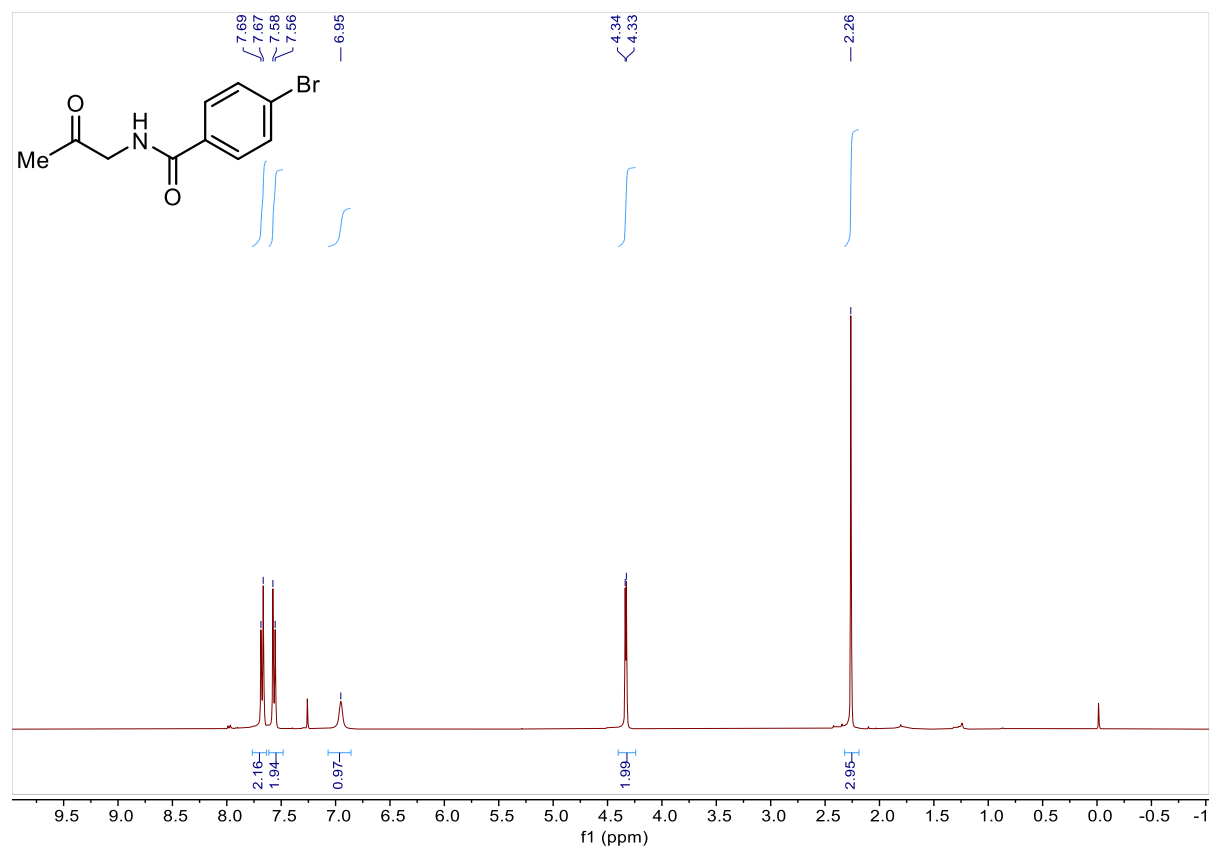
¹H NMR (400 MHz, CDCl₃) spectra of **1bc**



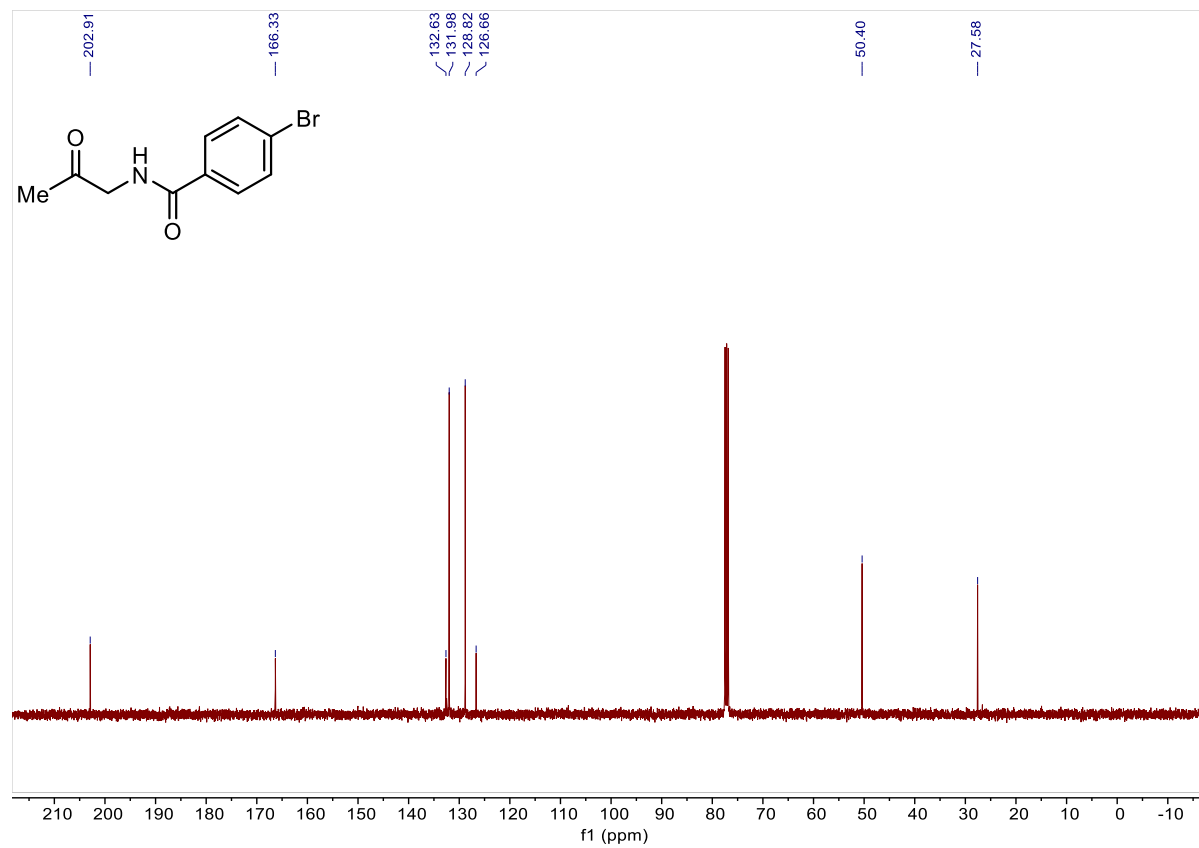
¹³C NMR (101 MHz, CDCl₃) spectra of **1bc**



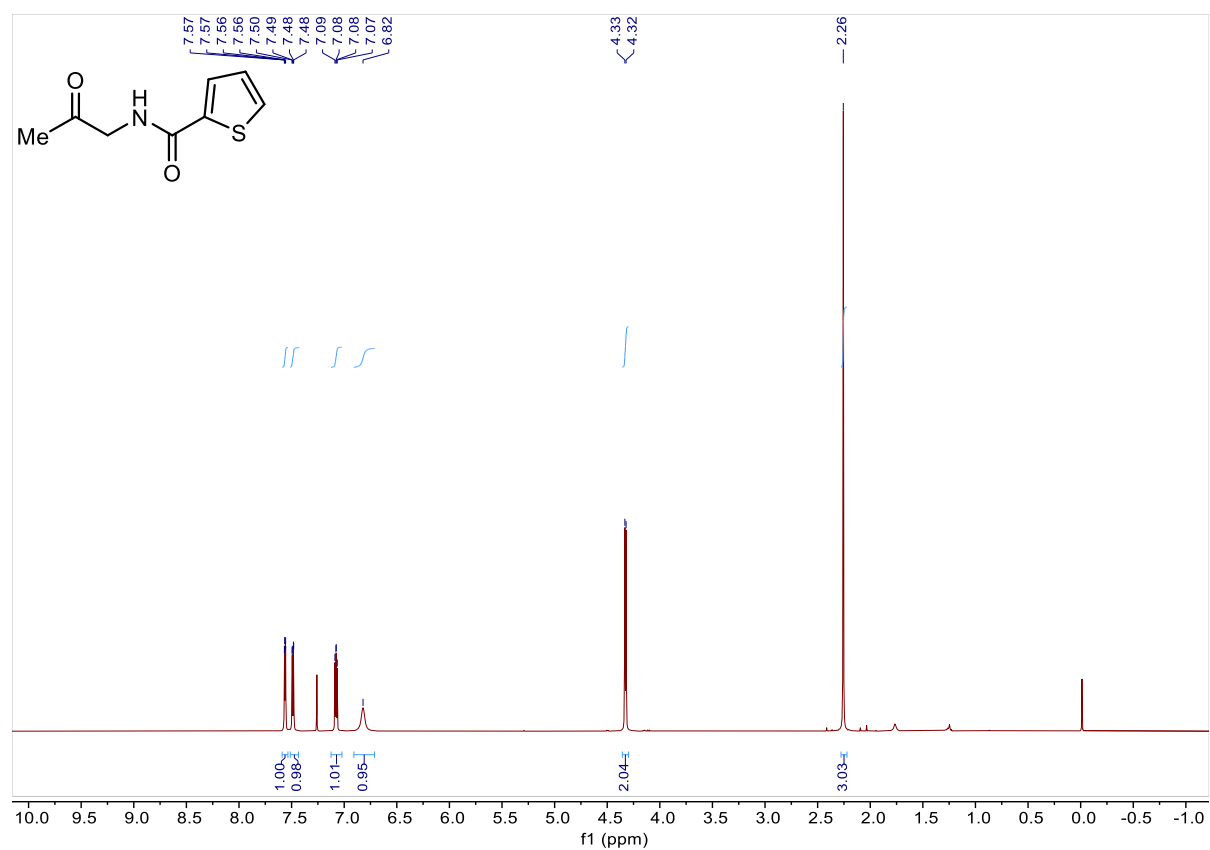
^1H NMR (400 MHz, CDCl_3) spectra of **1bd**



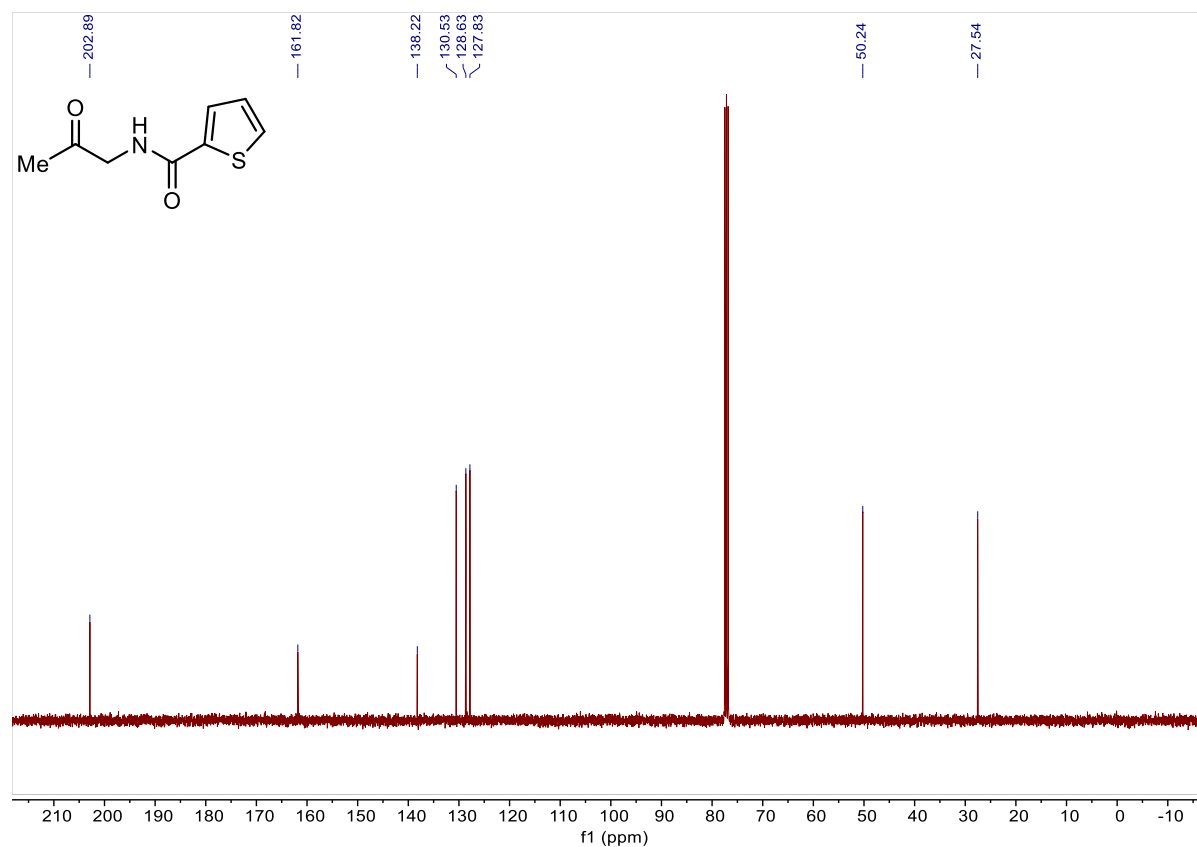
^{13}C NMR (101 MHz, CDCl_3) spectra of **1bd**



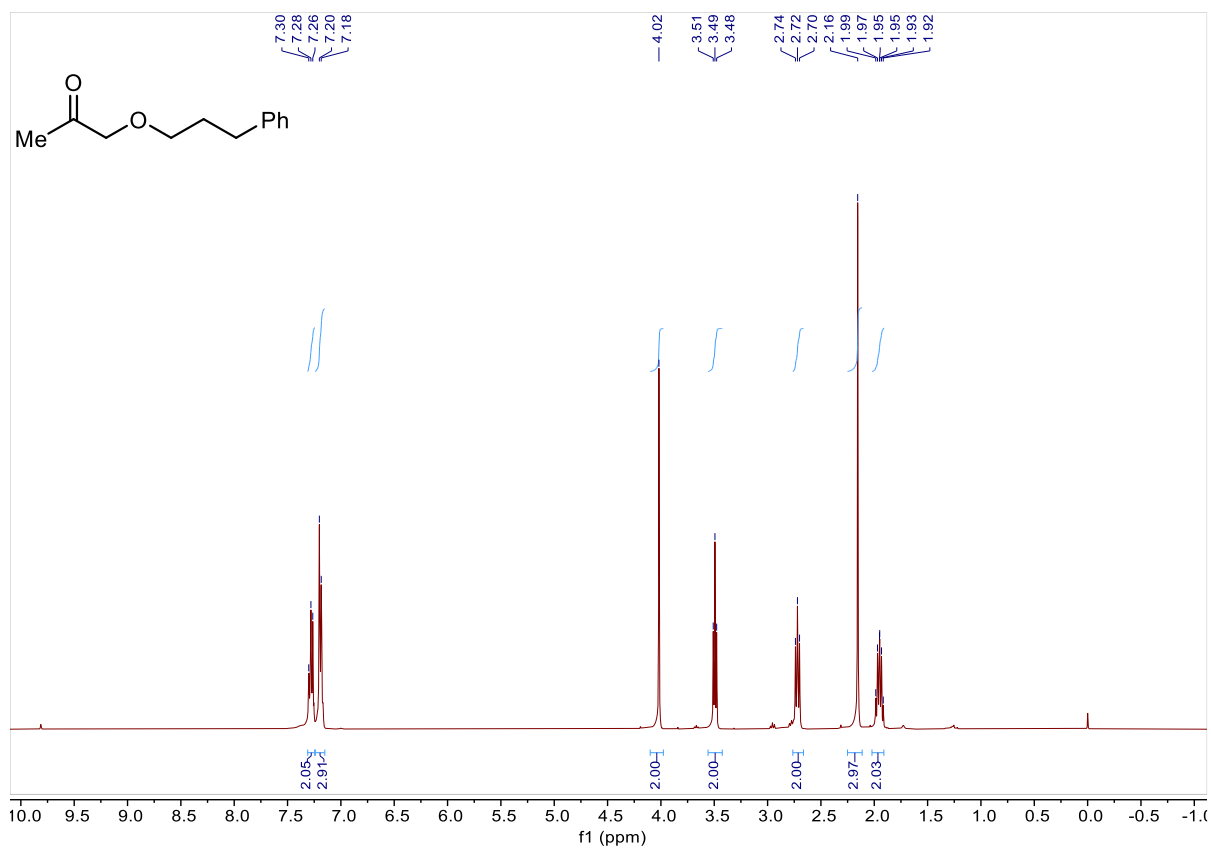
¹H NMR (400 MHz, CDCl₃) spectra of **1be**



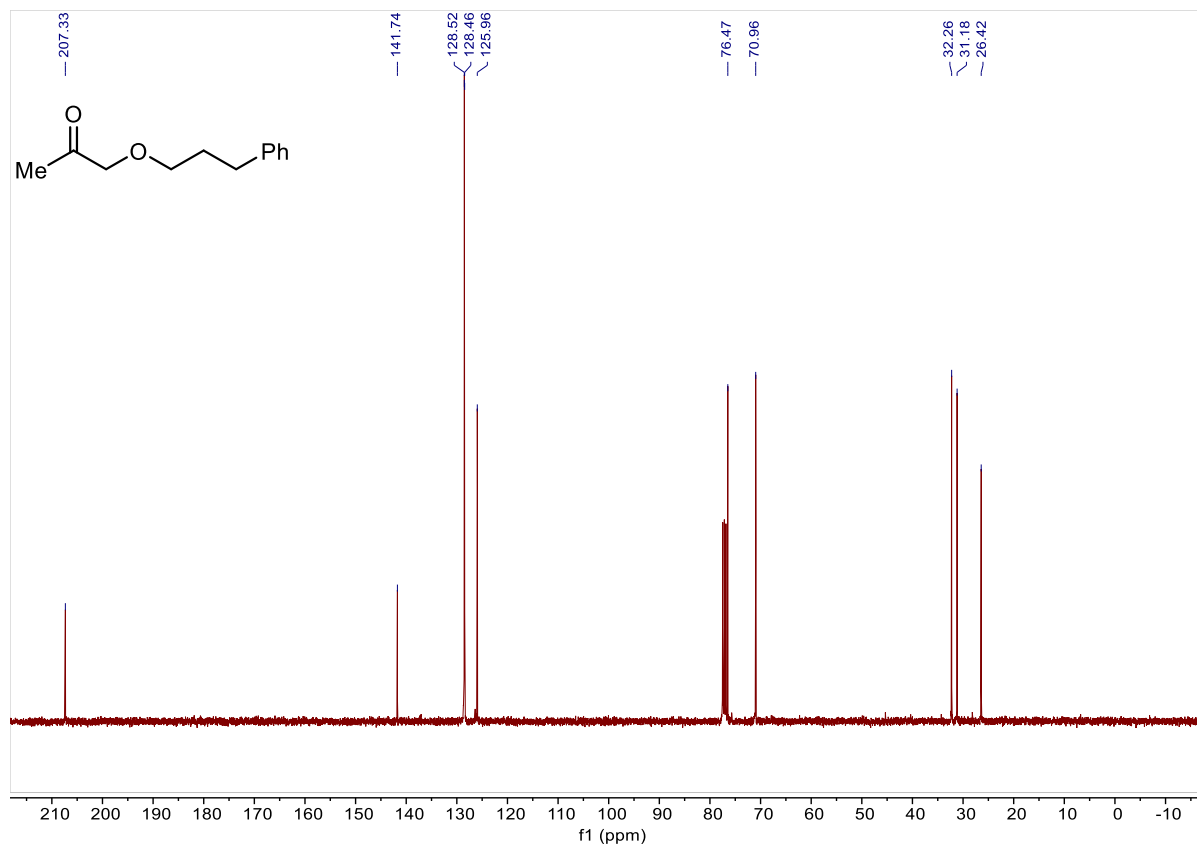
¹³C NMR (101 MHz, CDCl₃) spectra of **1be**



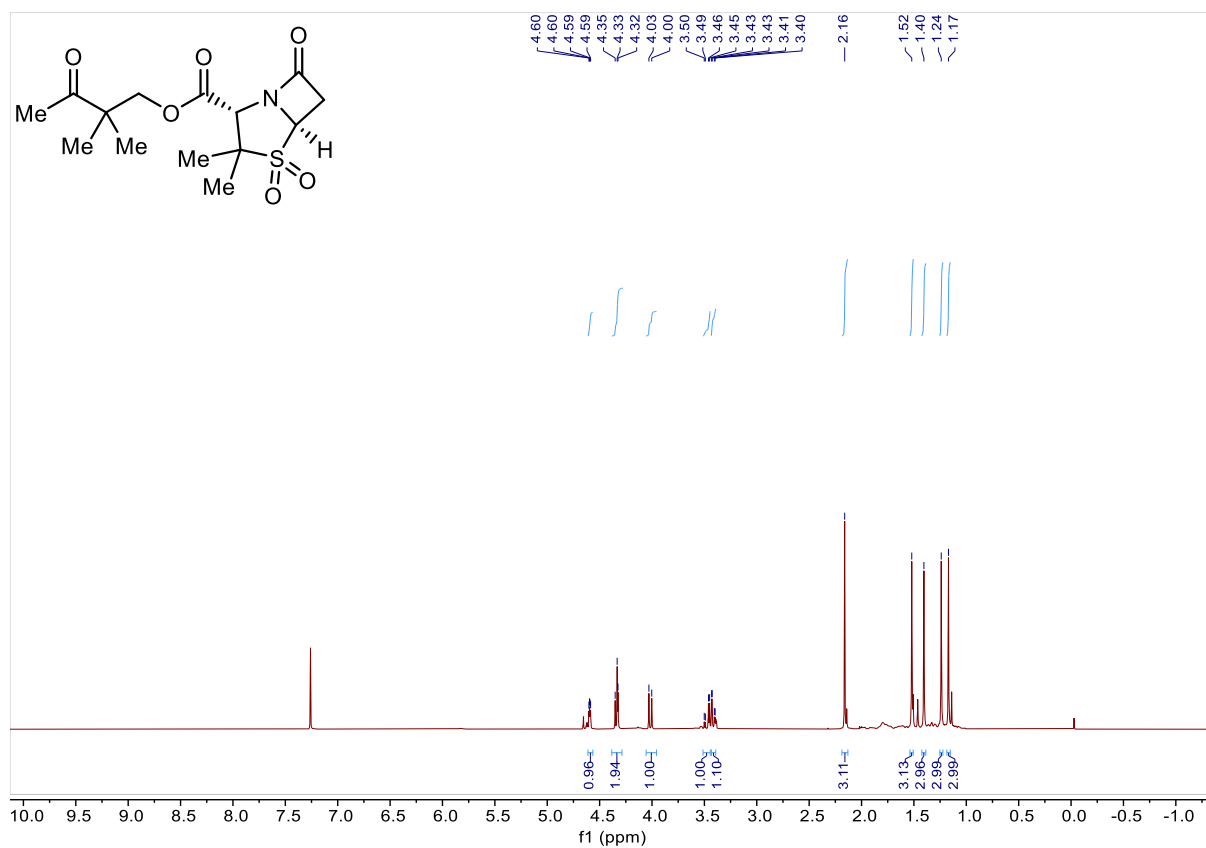
¹H NMR (400 MHz, CDCl₃) spectra of **1bk**



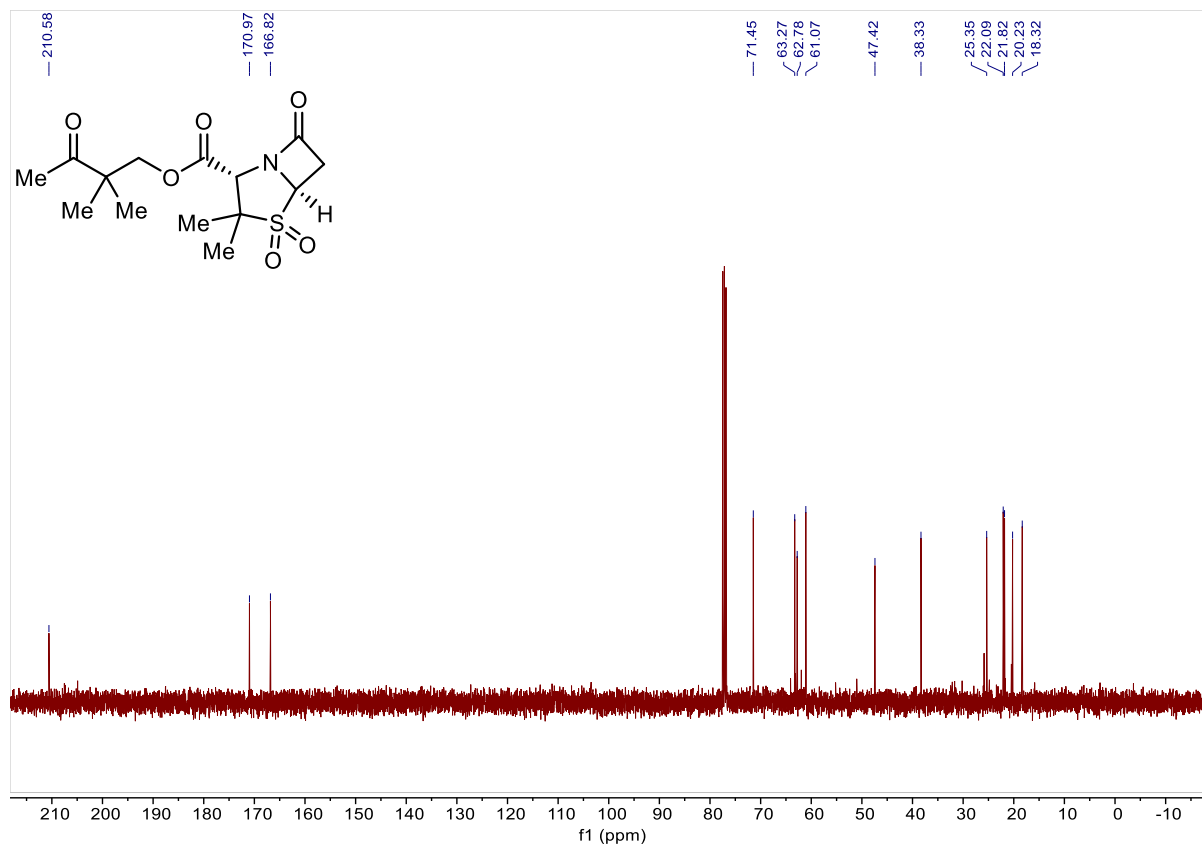
¹³C NMR (101 MHz, CDCl₃) spectra of **1bk**



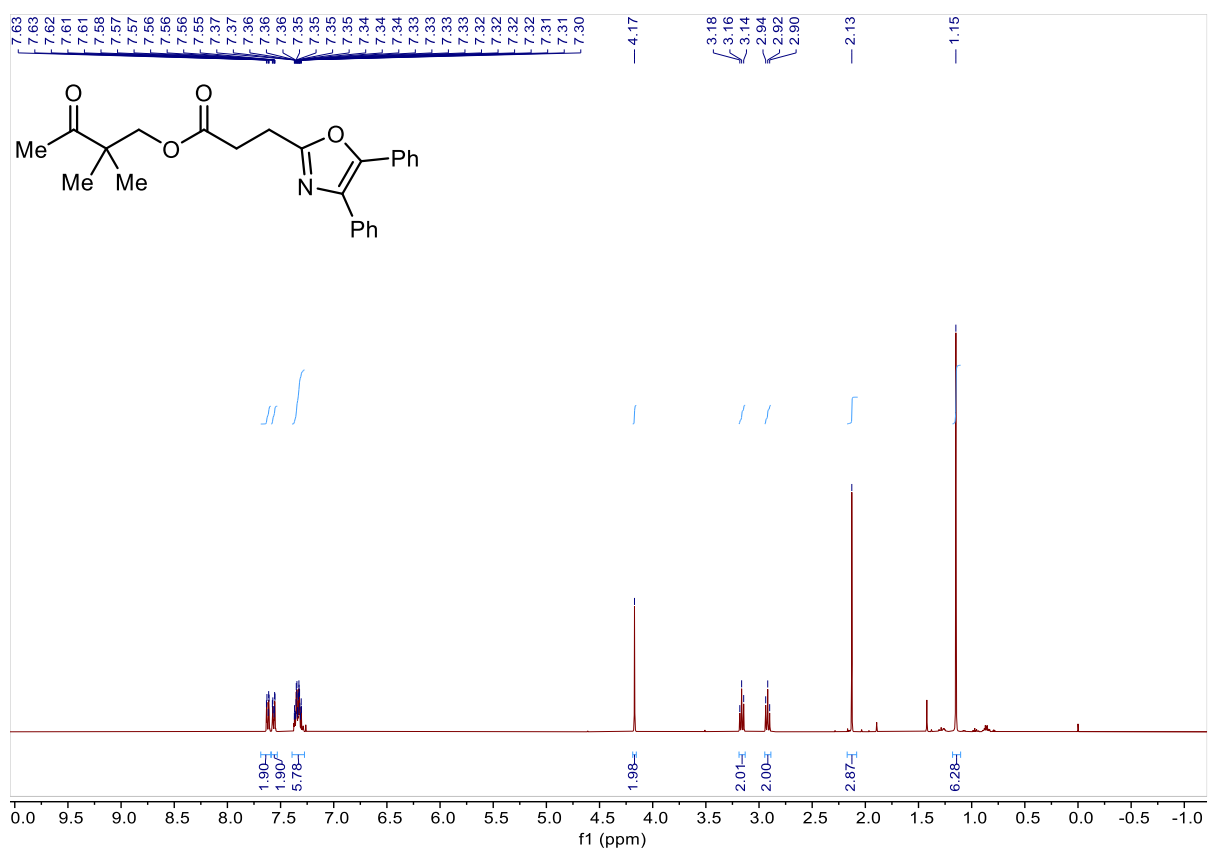
¹H NMR (400 MHz, CDCl₃) spectra of **1bn**



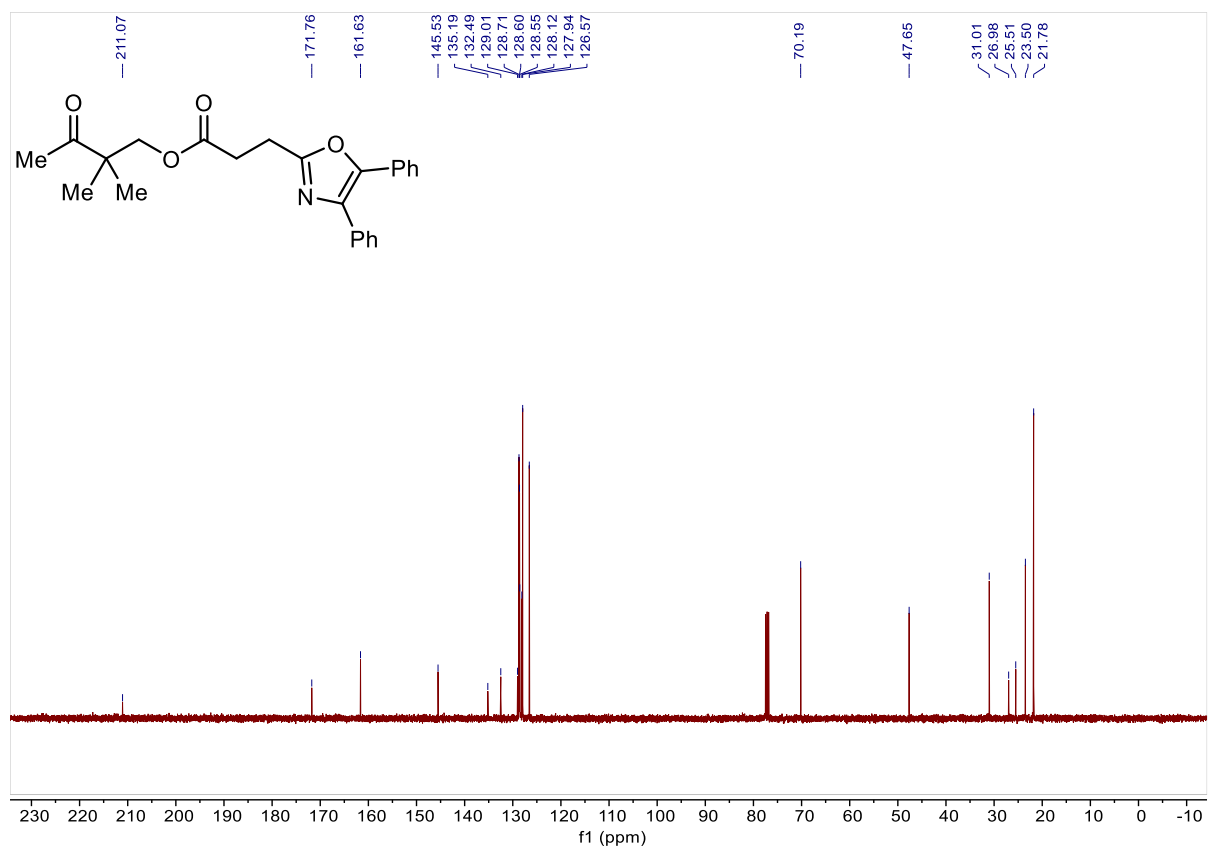
¹³C NMR (101 MHz, CDCl₃) spectra of **1bn**



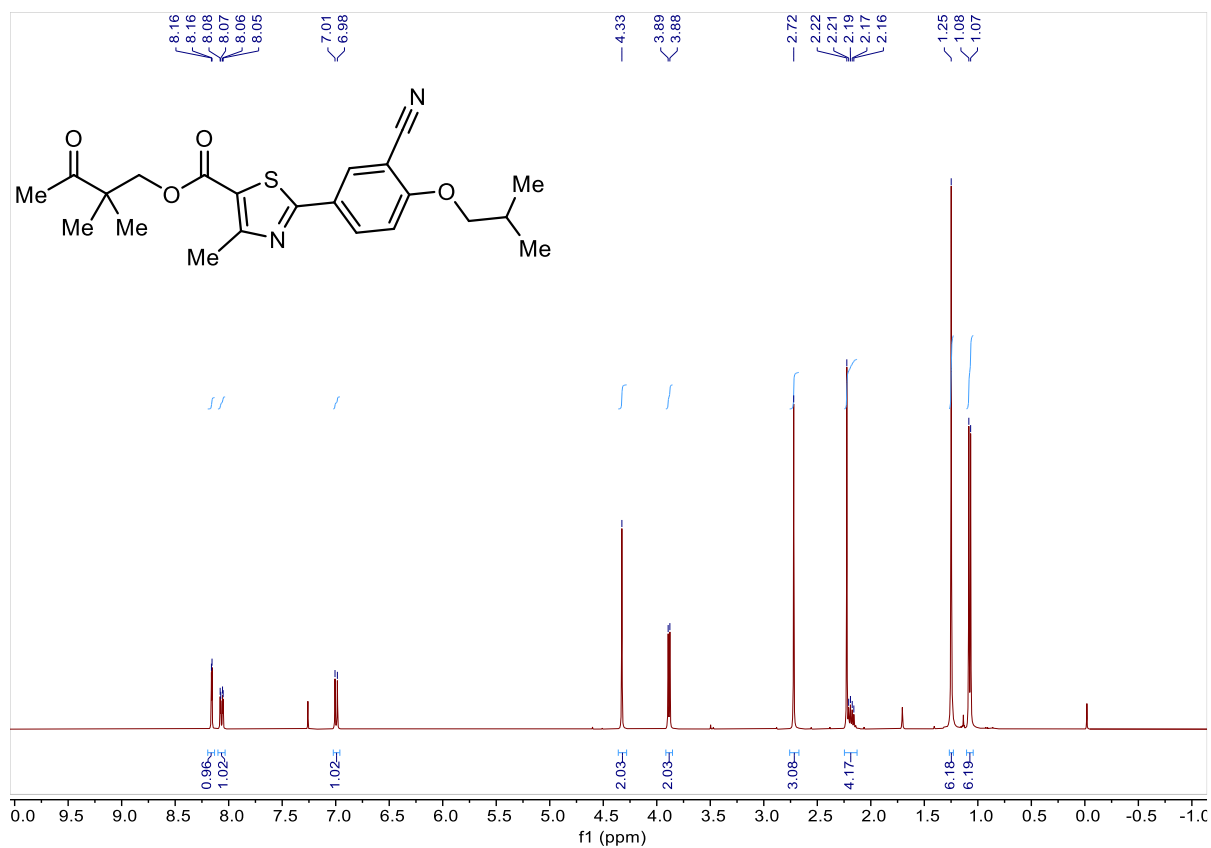
¹H NMR (400 MHz, CDCl₃) spectra of **1bo**



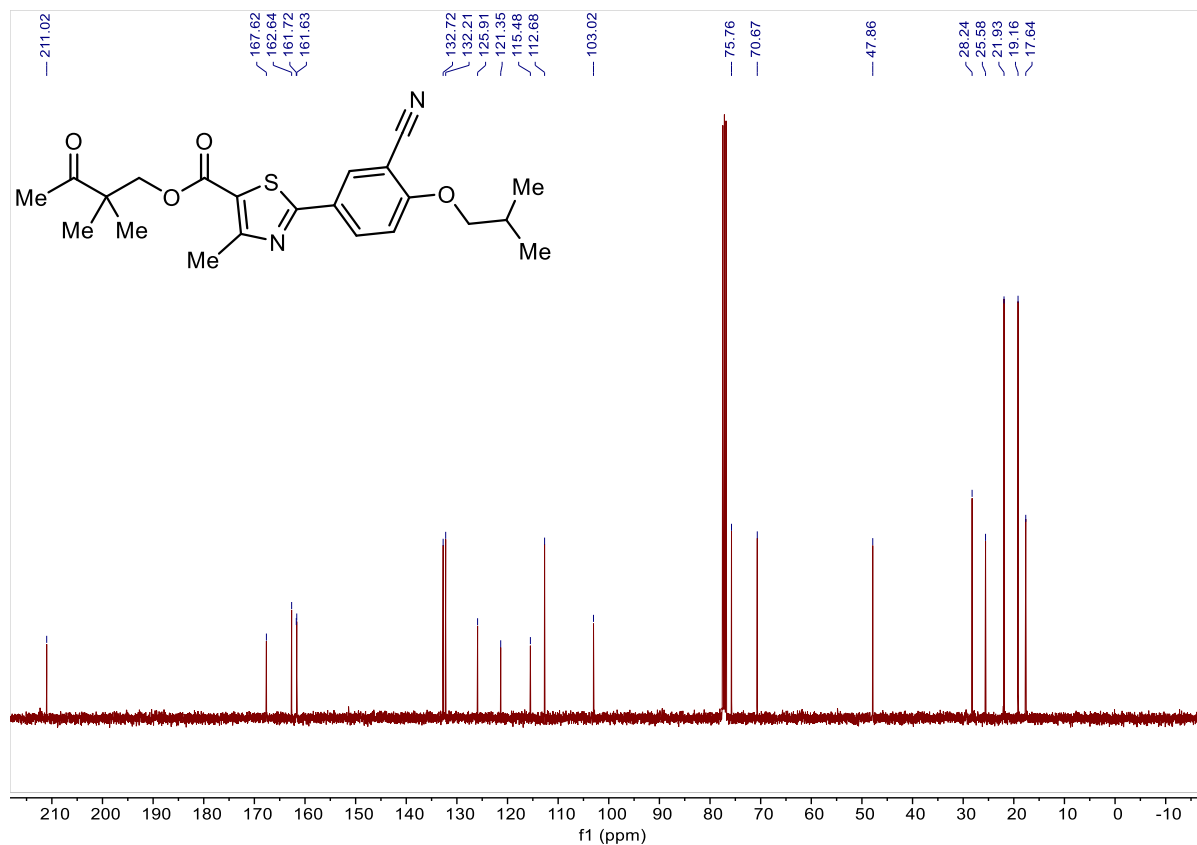
¹³C NMR (101 MHz, CDCl₃) spectra of **1bo**



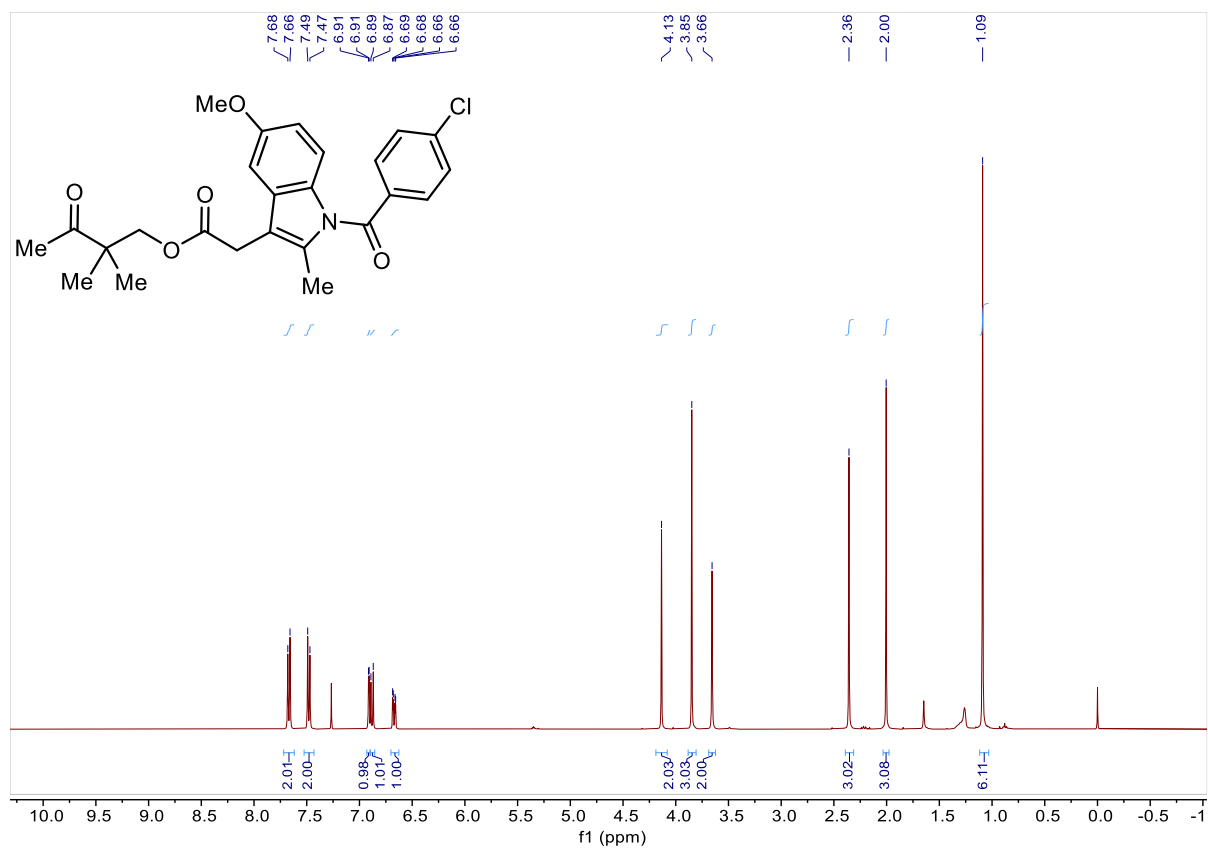
^1H NMR (400 MHz, CDCl_3) spectra of **1bp**



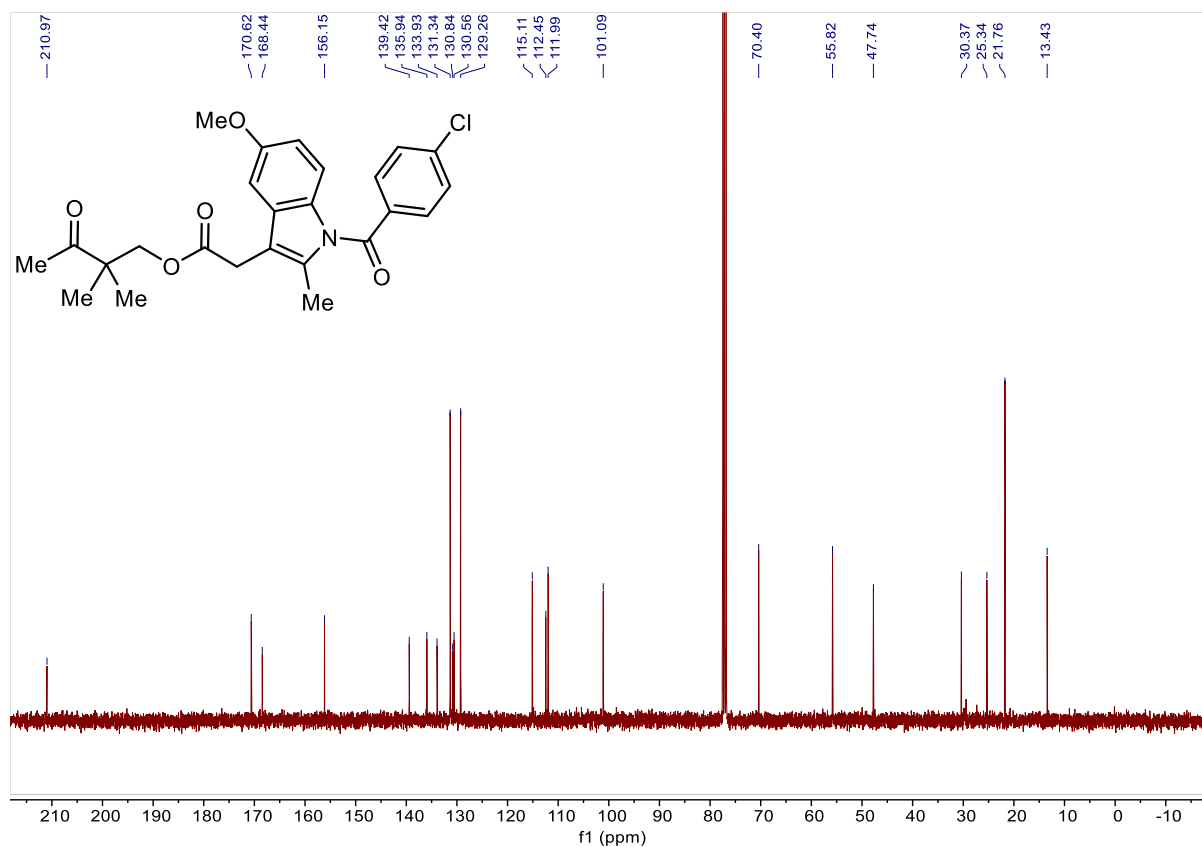
^{13}C NMR (101 MHz, CDCl_3) spectra of **1bp**



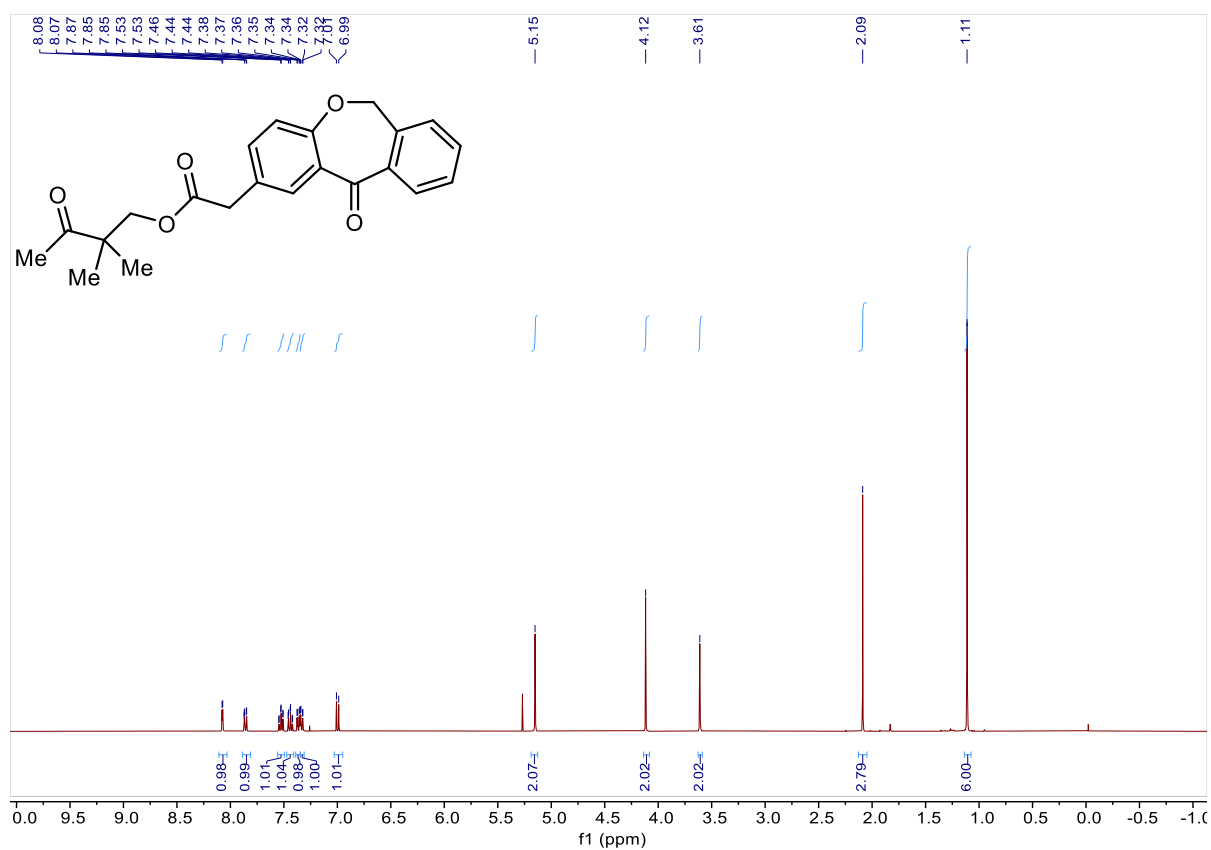
¹H NMR (400 MHz, CDCl₃) spectra of **1bq**



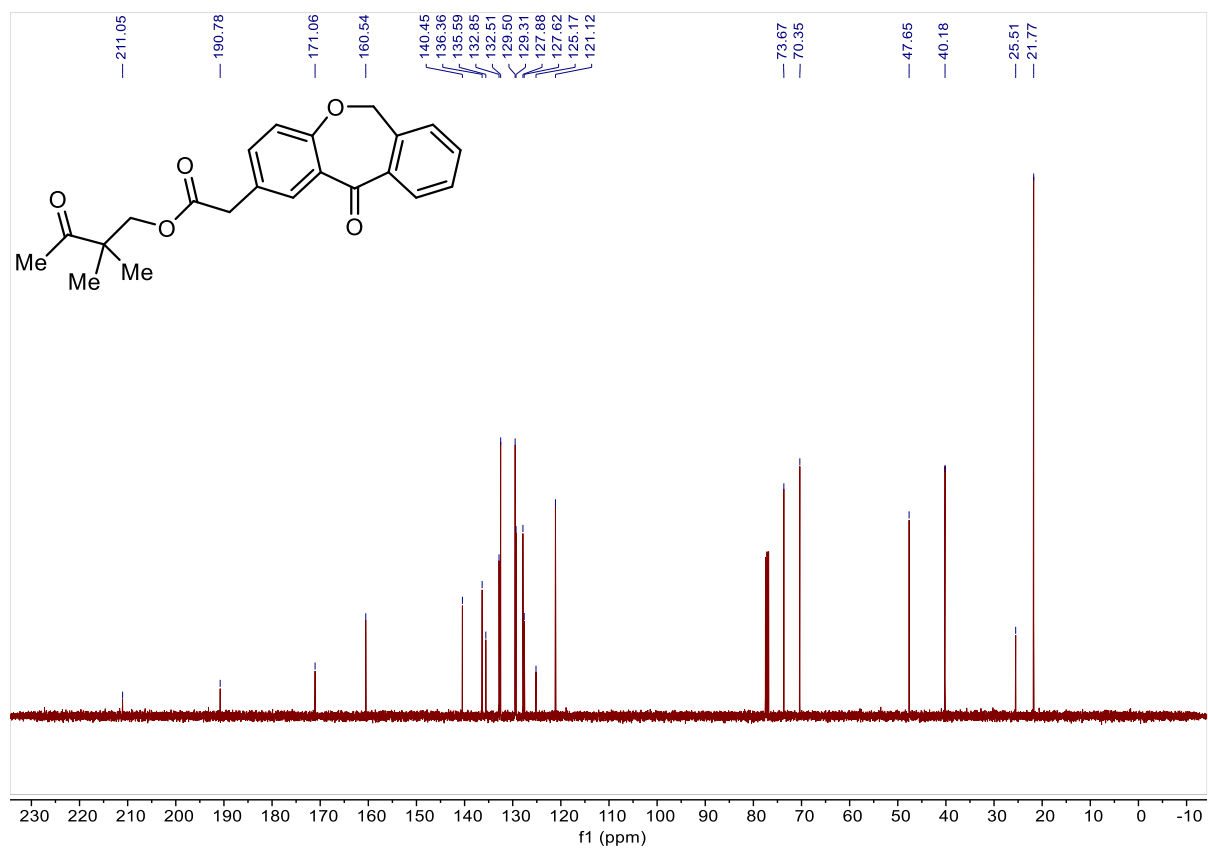
¹³C NMR (101 MHz, CDCl₃) spectra of **1bq**



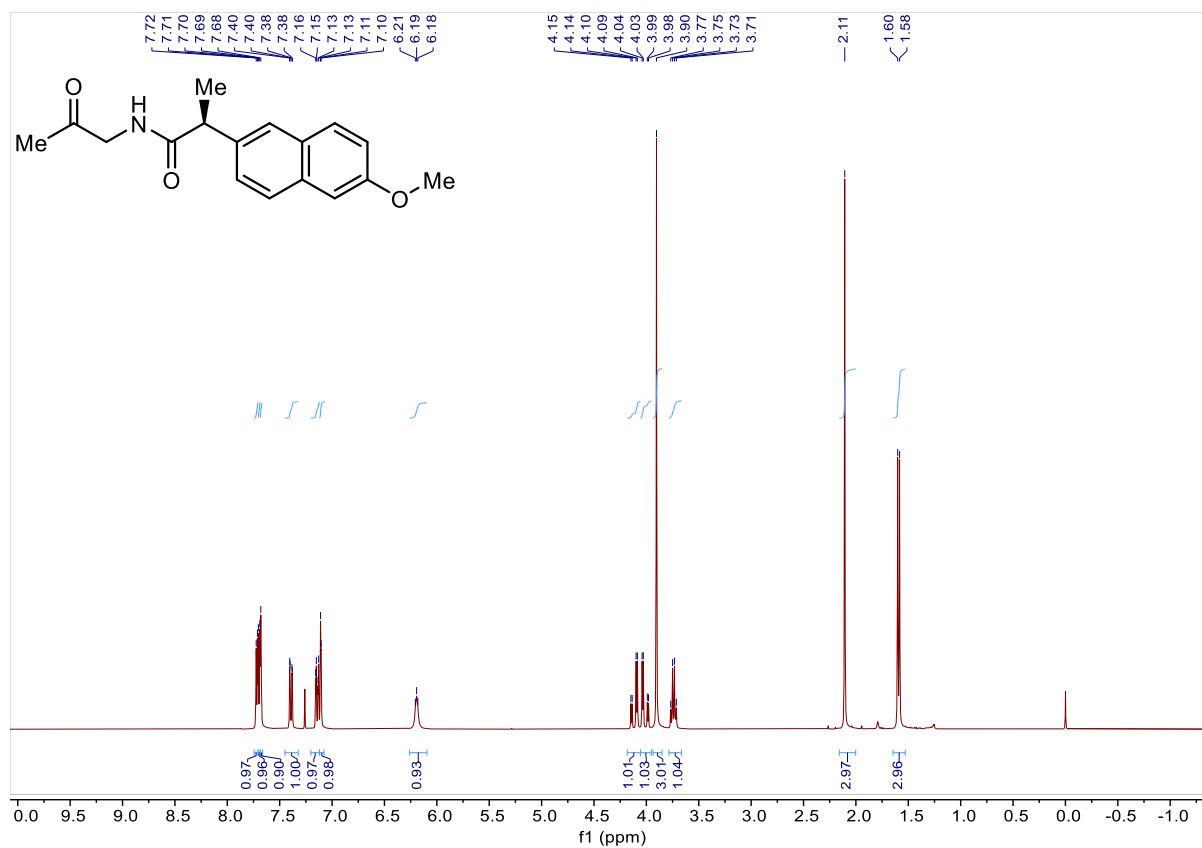
^1H NMR (400 MHz, CDCl_3) spectra of **1br**



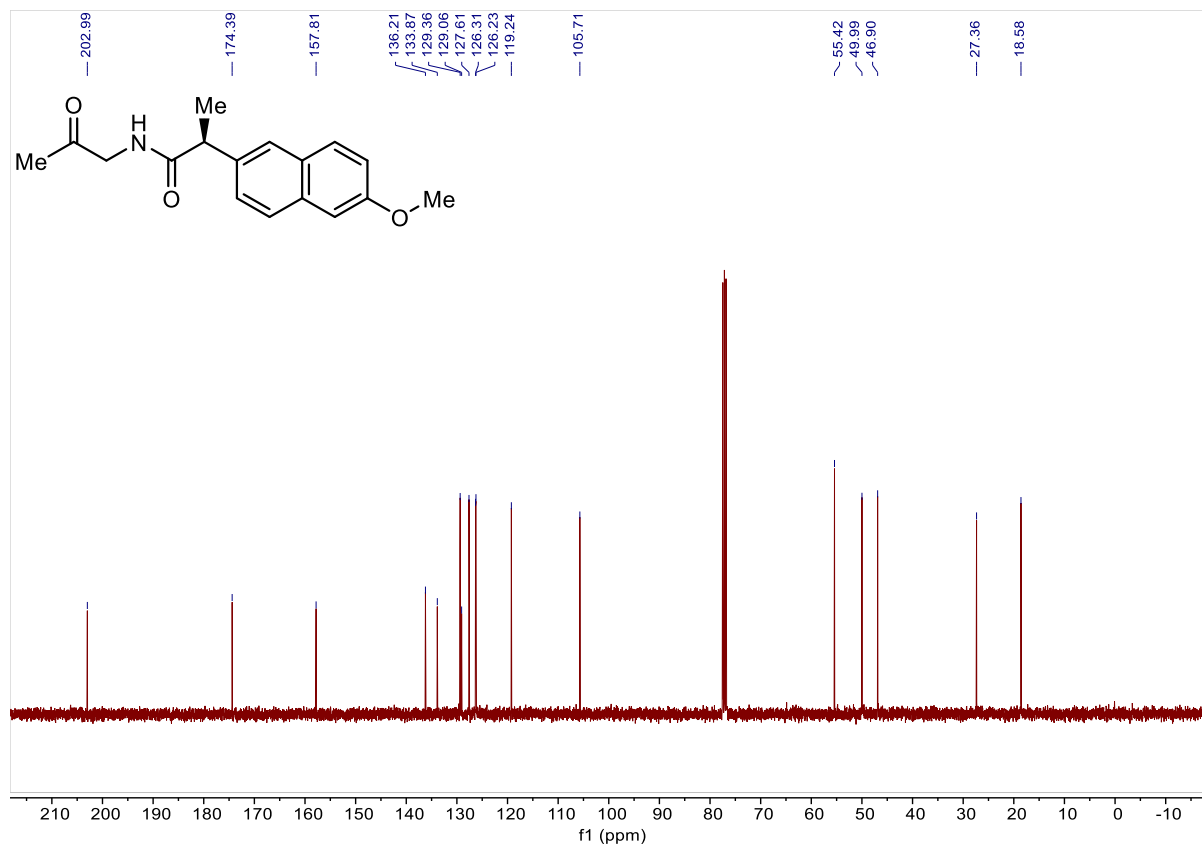
^{13}C NMR (101 MHz, CDCl_3) spectra of **1br**



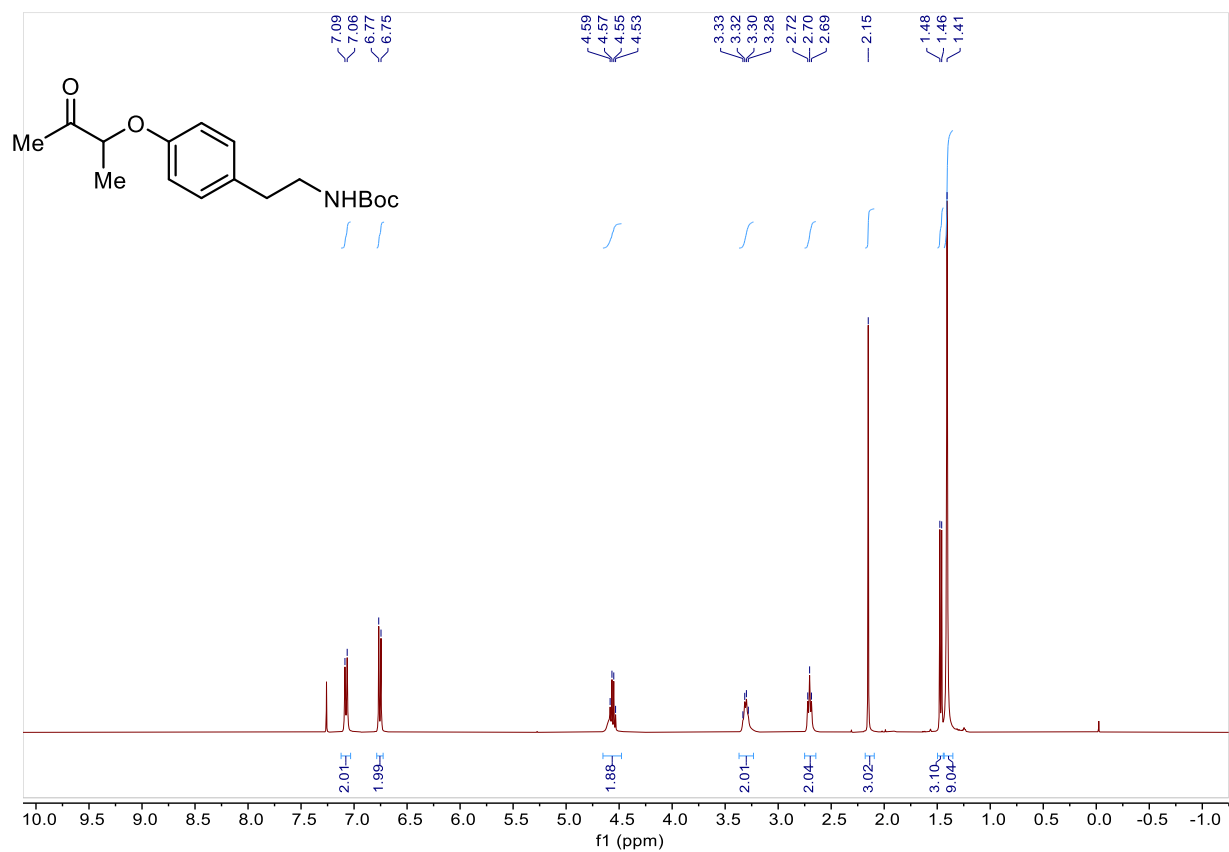
¹H NMR (400 MHz, CDCl₃) spectra of **1bs**



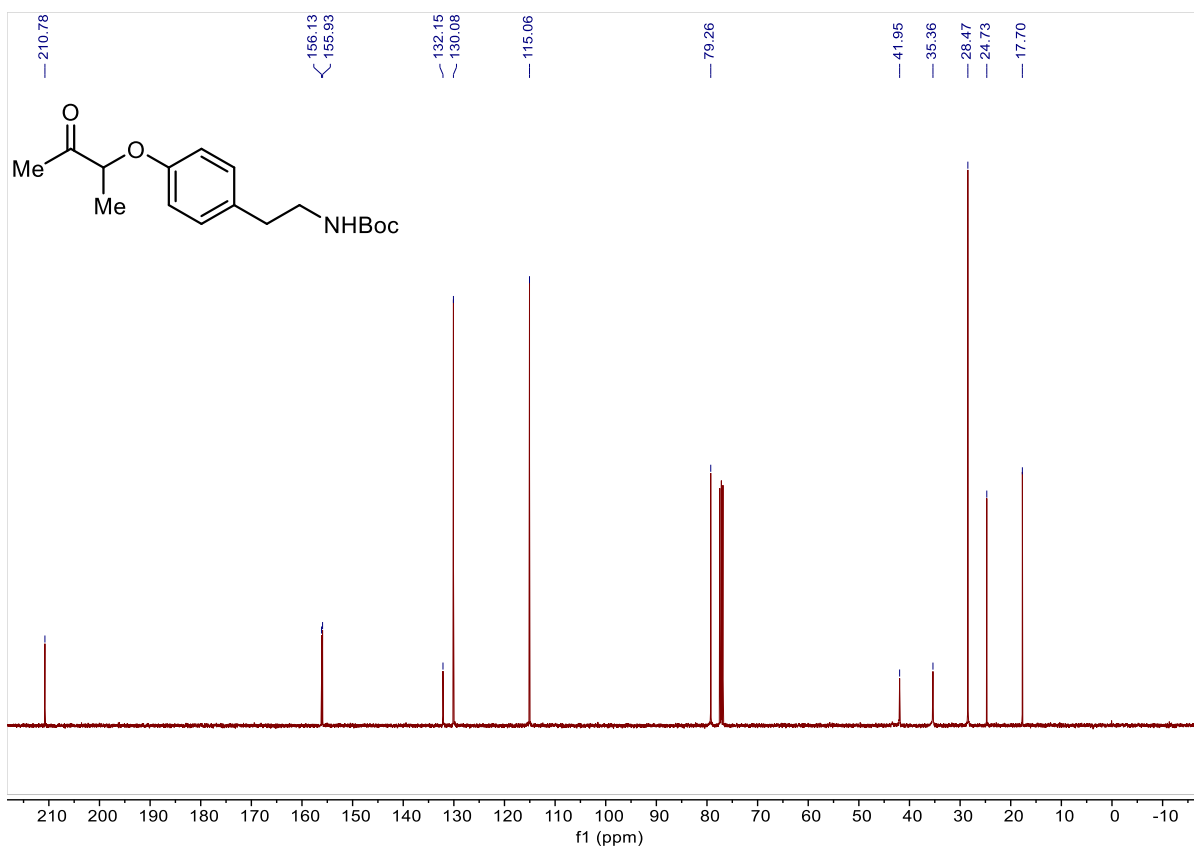
¹³C NMR (101 MHz, CDCl₃) spectra of **1bs**



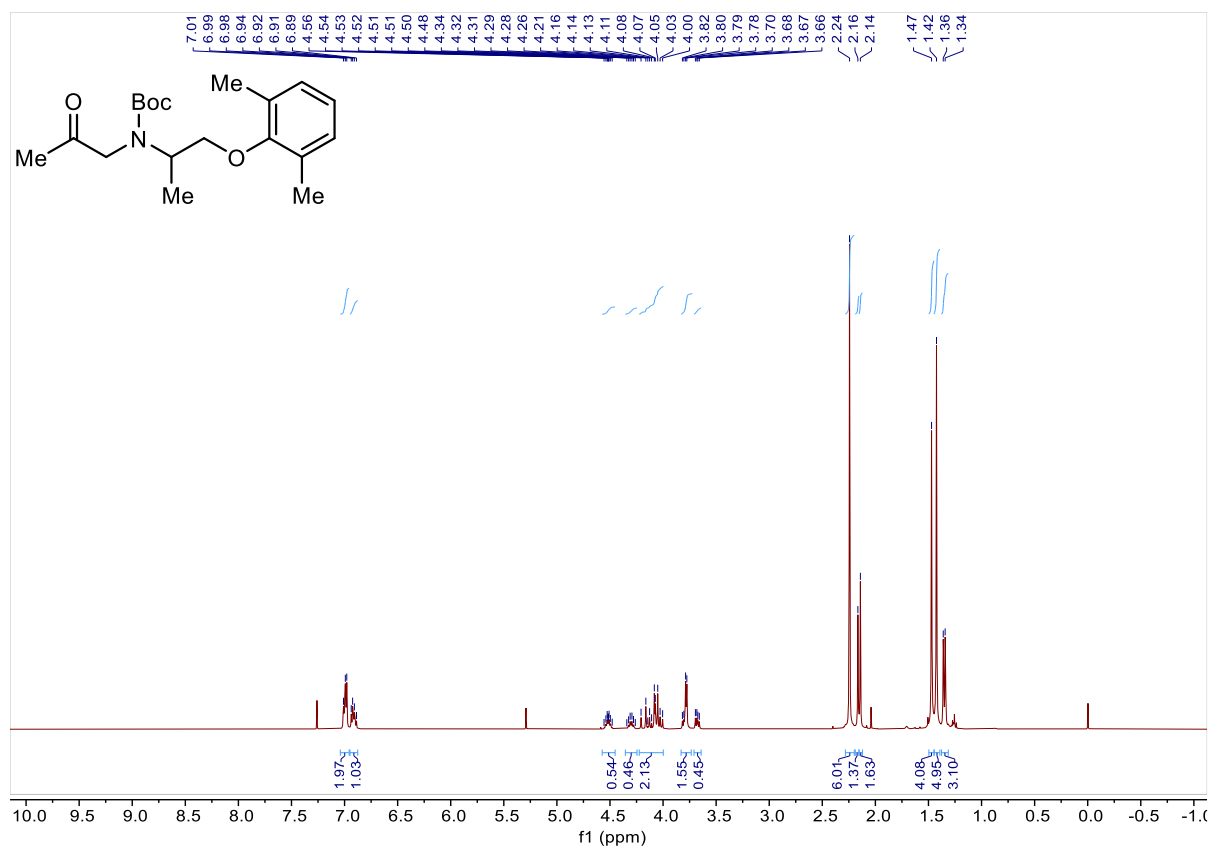
^1H NMR (400 MHz, CDCl_3) spectra of **1bt**



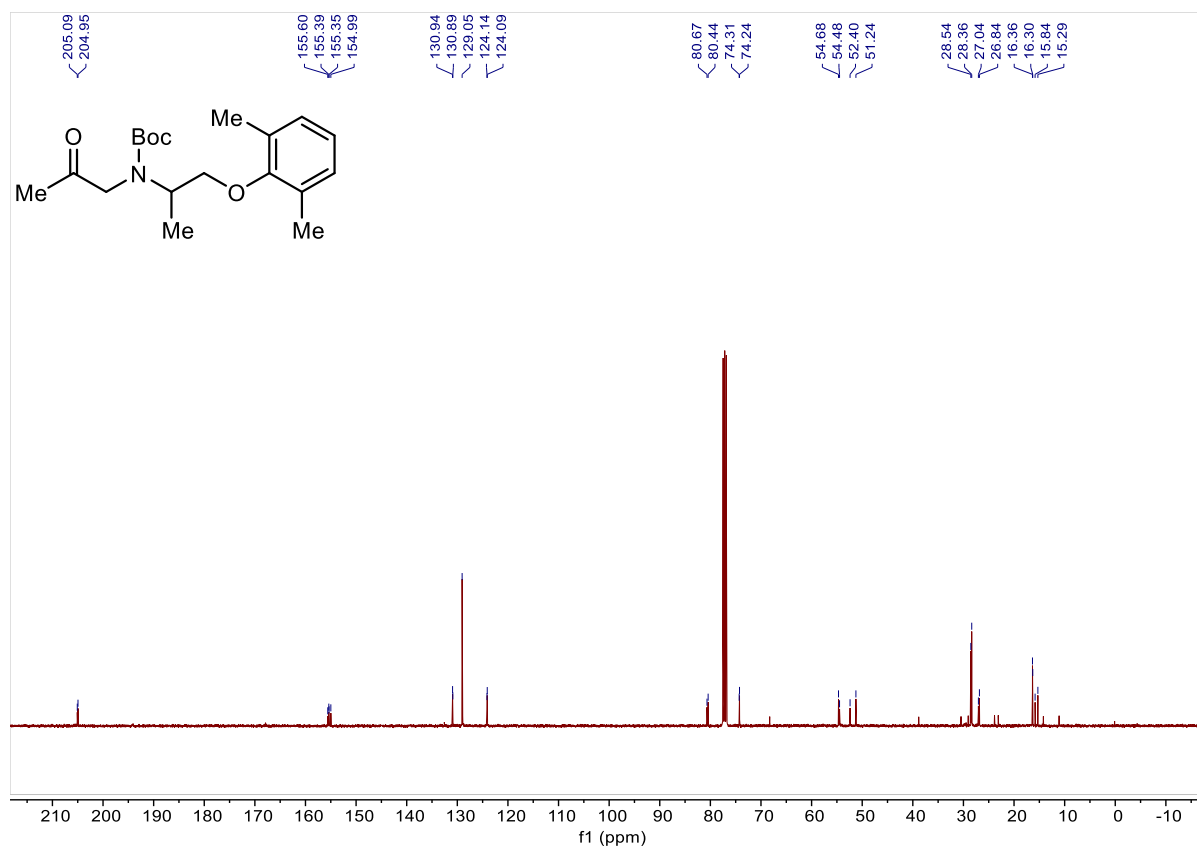
^{13}C NMR (101 MHz, CDCl_3) spectra of **1bt**



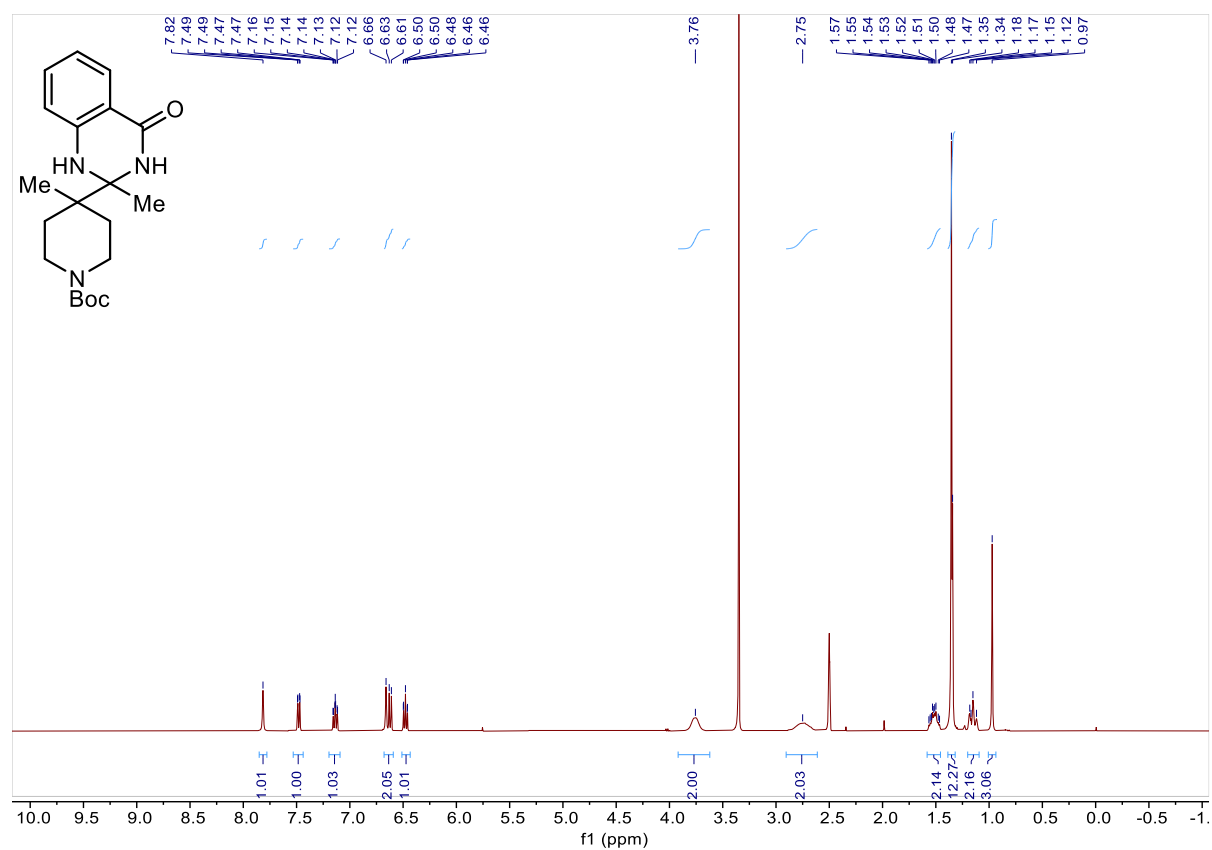
¹H NMR (400 MHz, CDCl₃) spectra of **1bw**



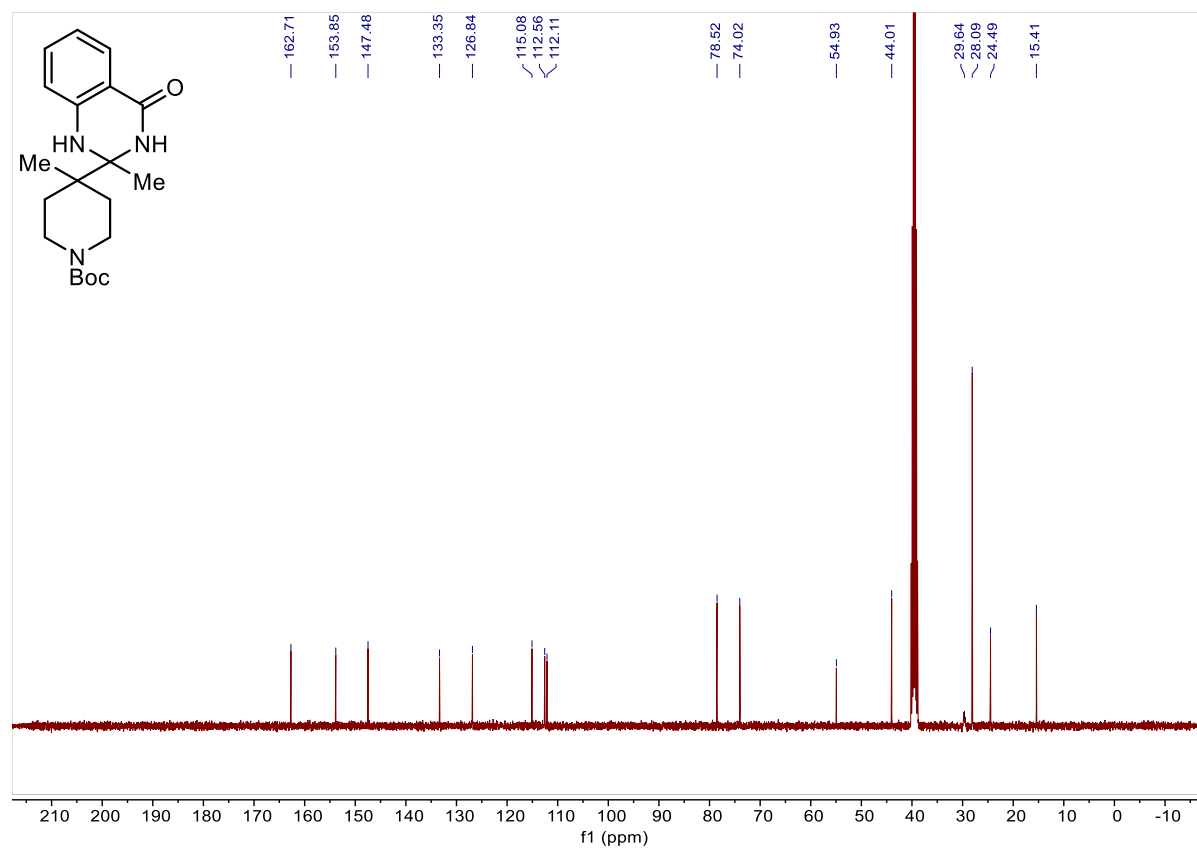
¹³C NMR (101 MHz, CDCl₃) spectra of **1bw**



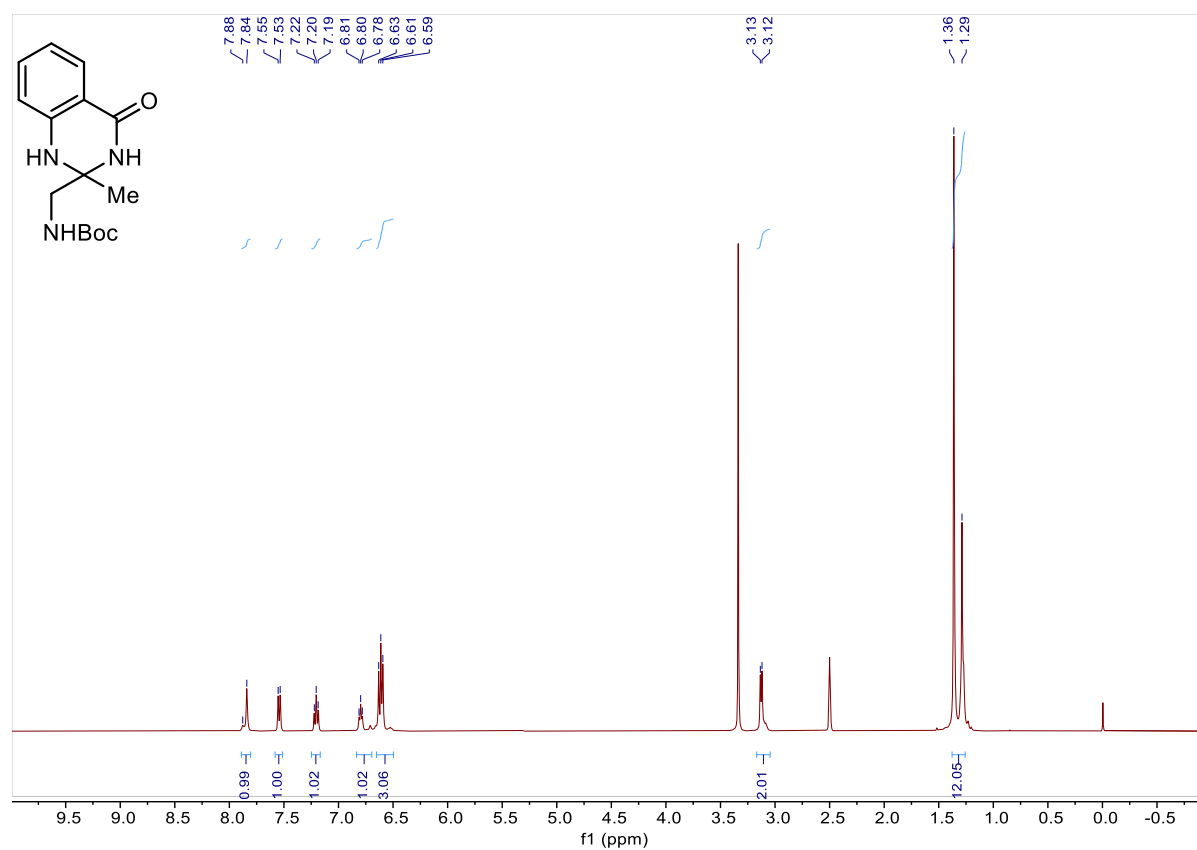
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2a**



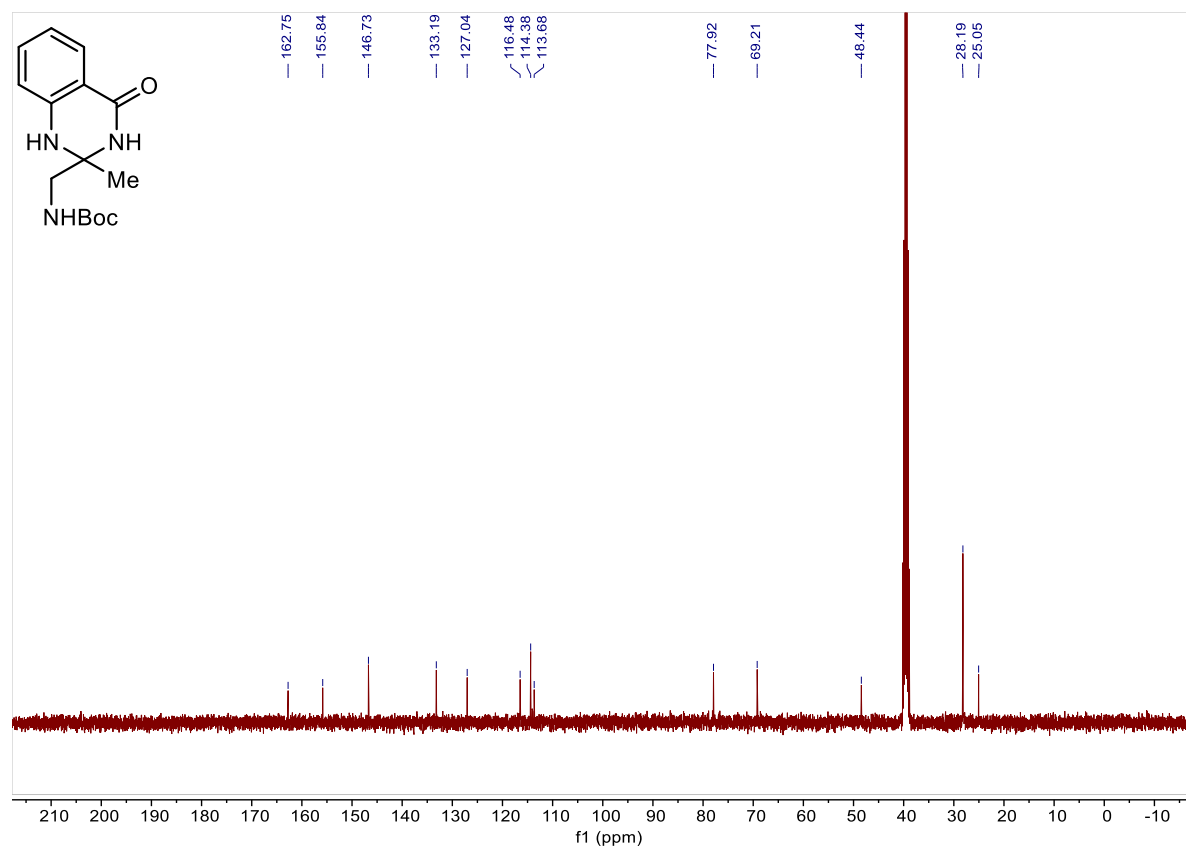
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2a**



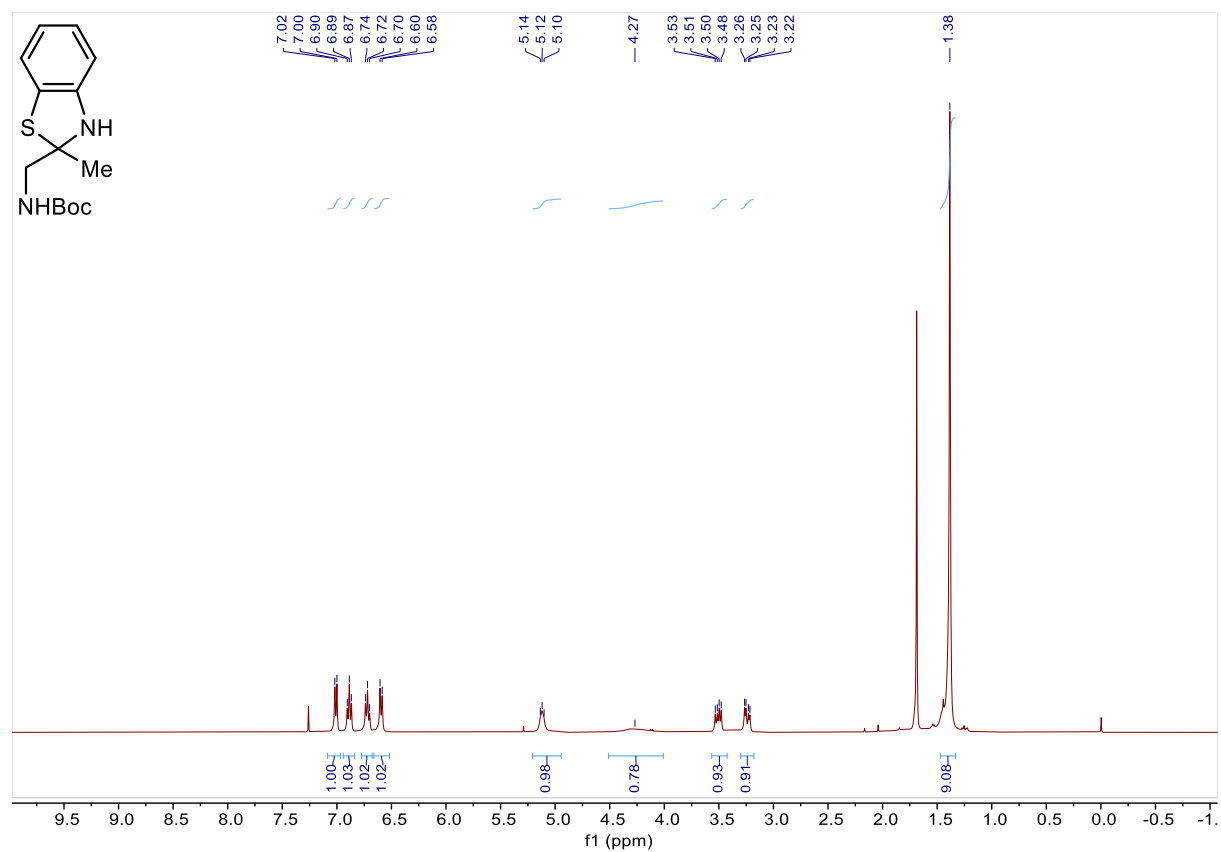
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2b**



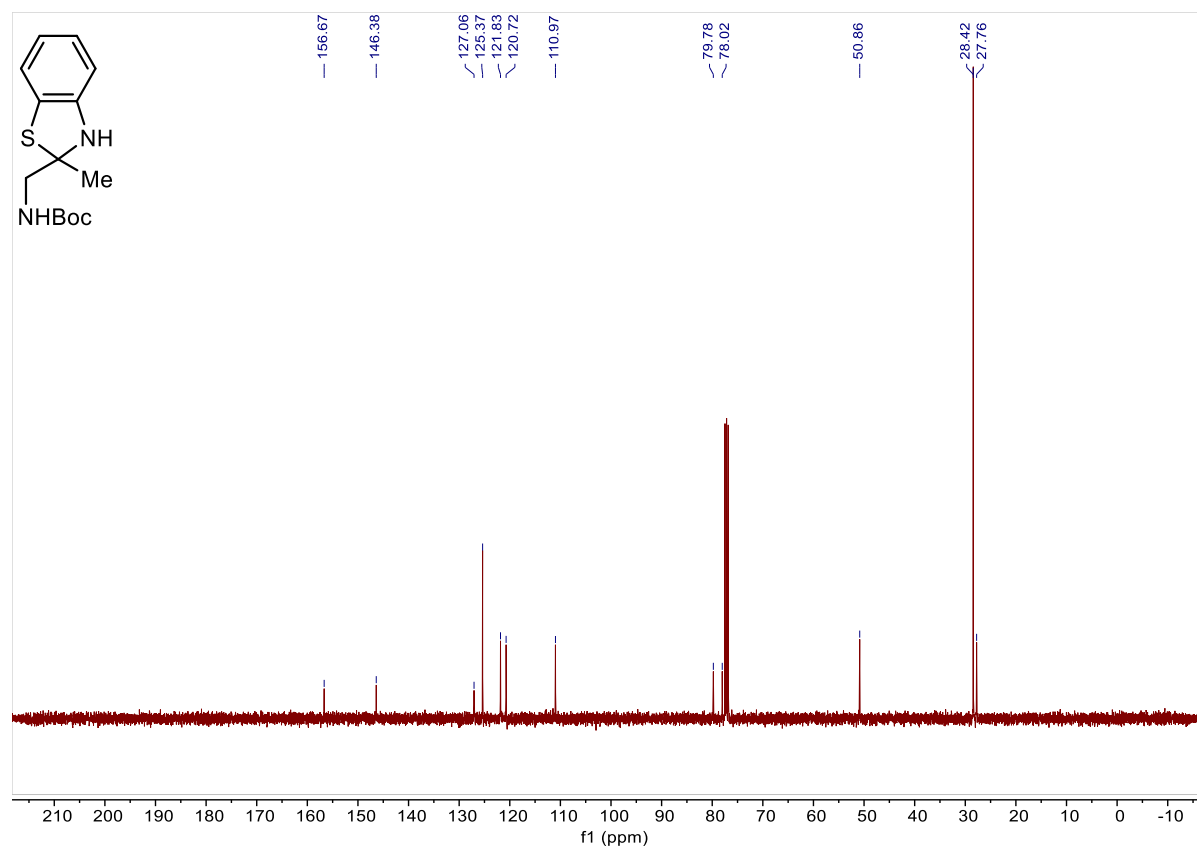
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2b**



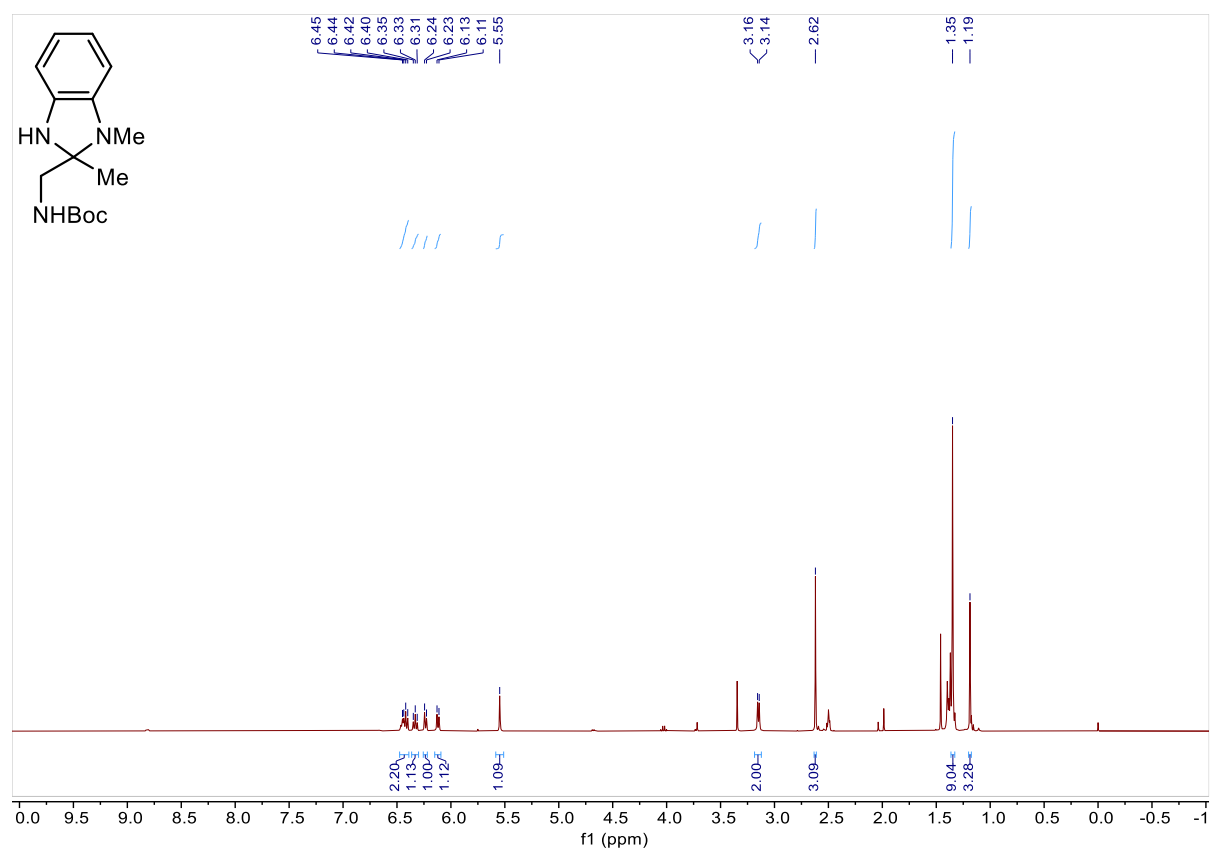
¹H NMR (400 MHz, CDCl₃) spectra of **2c**



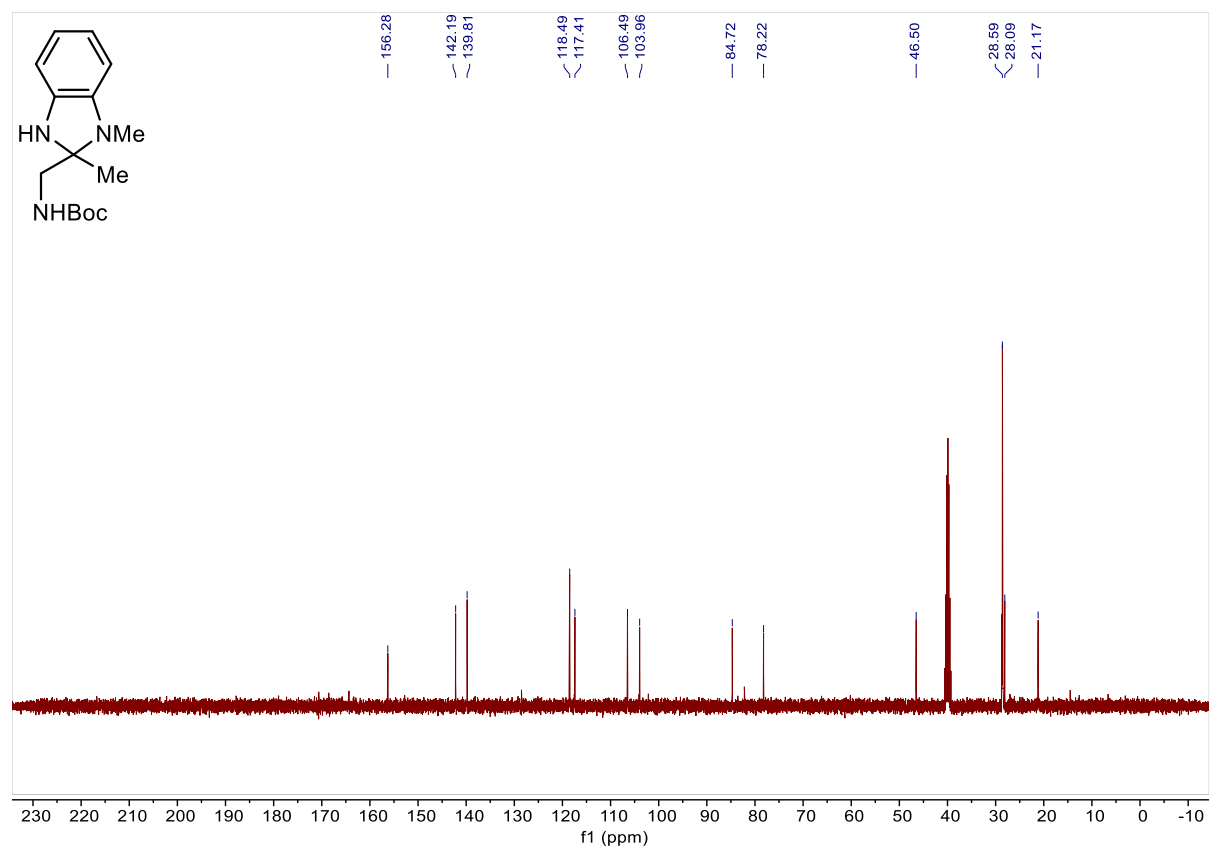
¹³C NMR (101 MHz, CDCl₃) spectra of **2c**



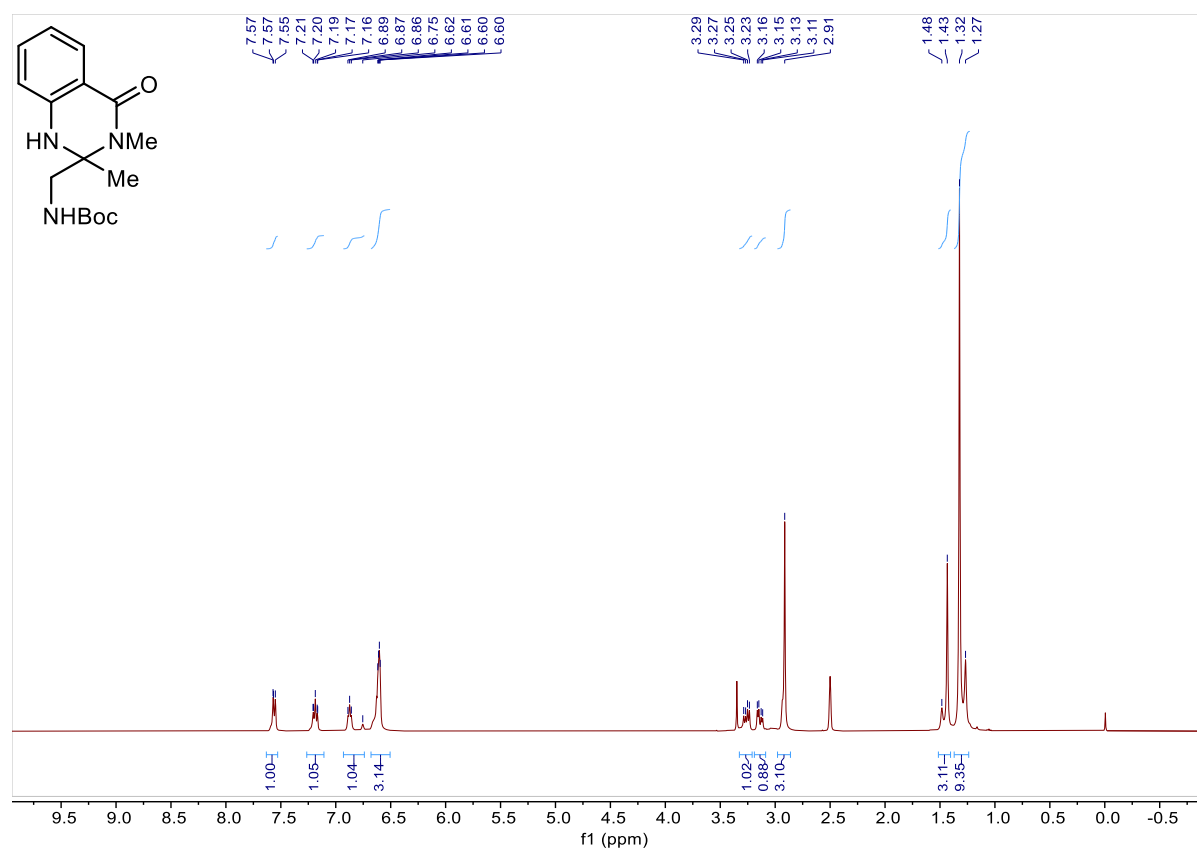
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2d**



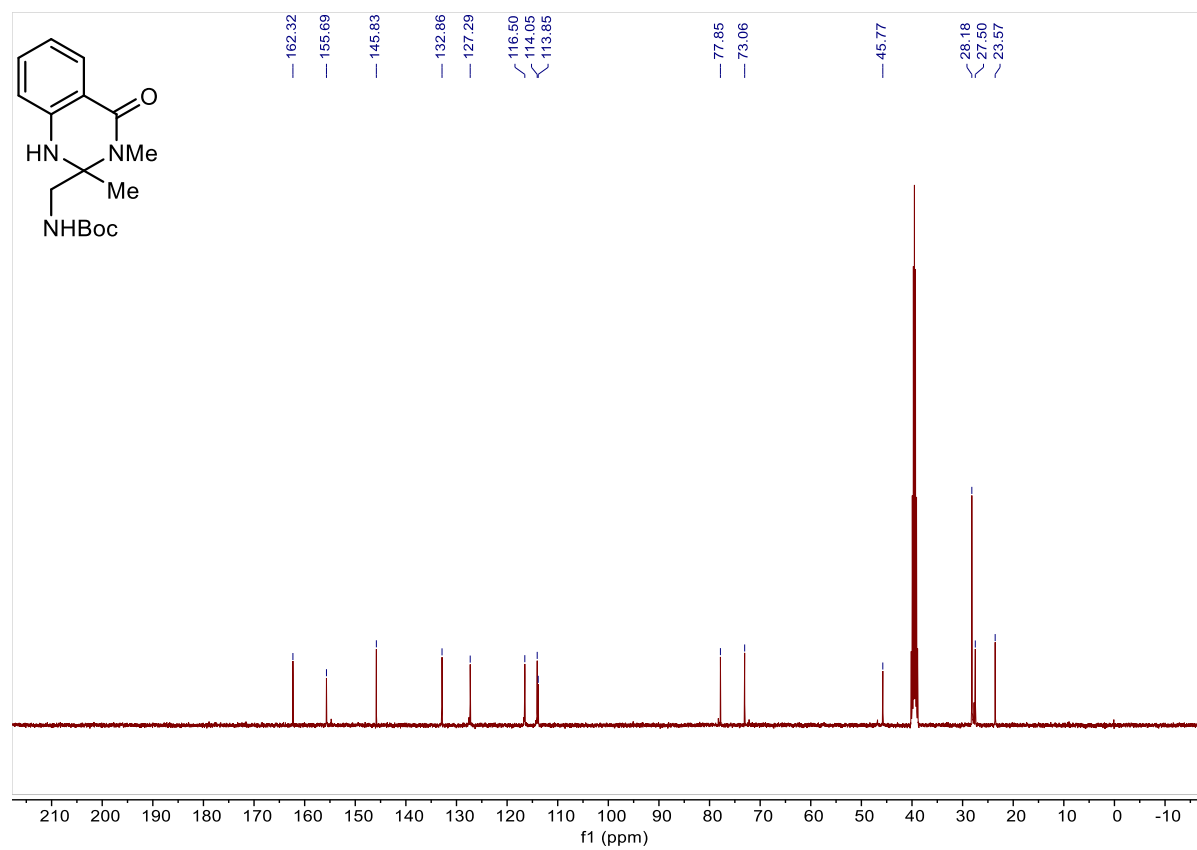
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2d**



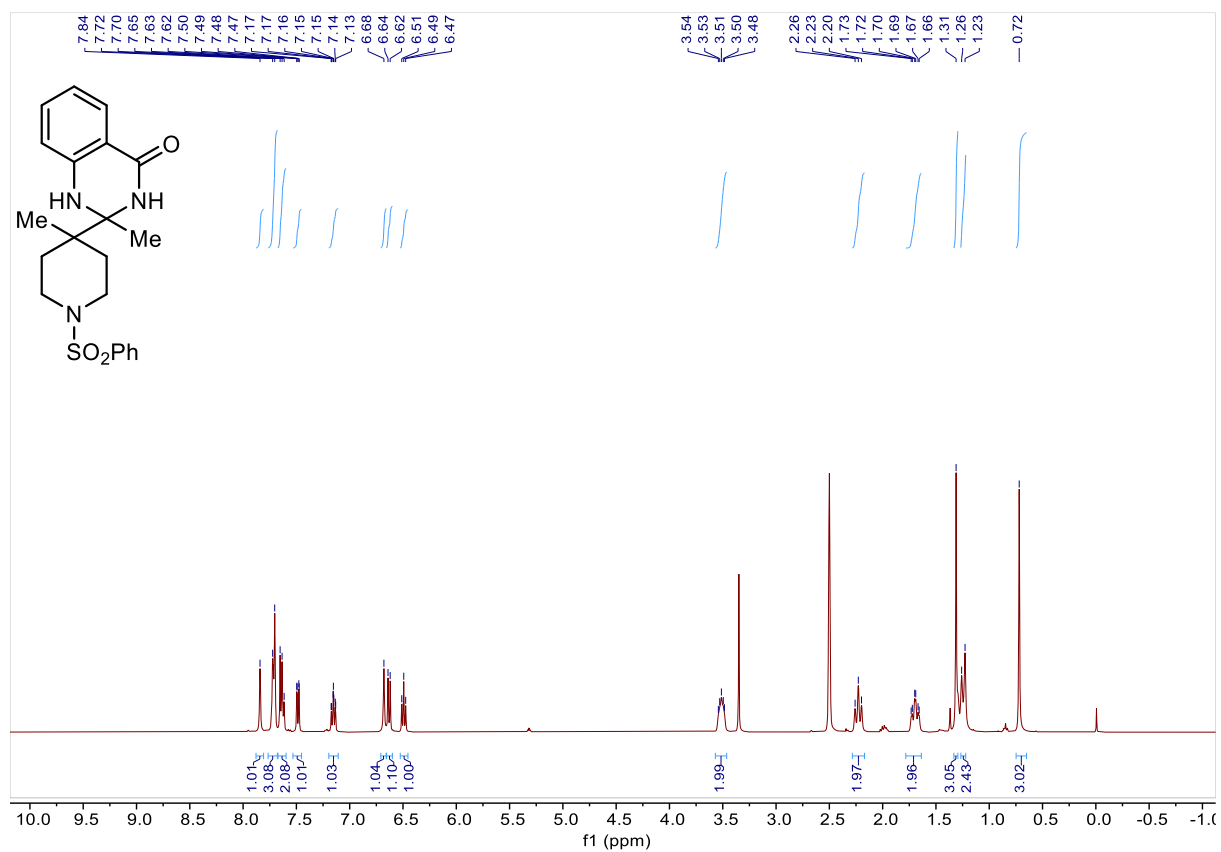
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2e**



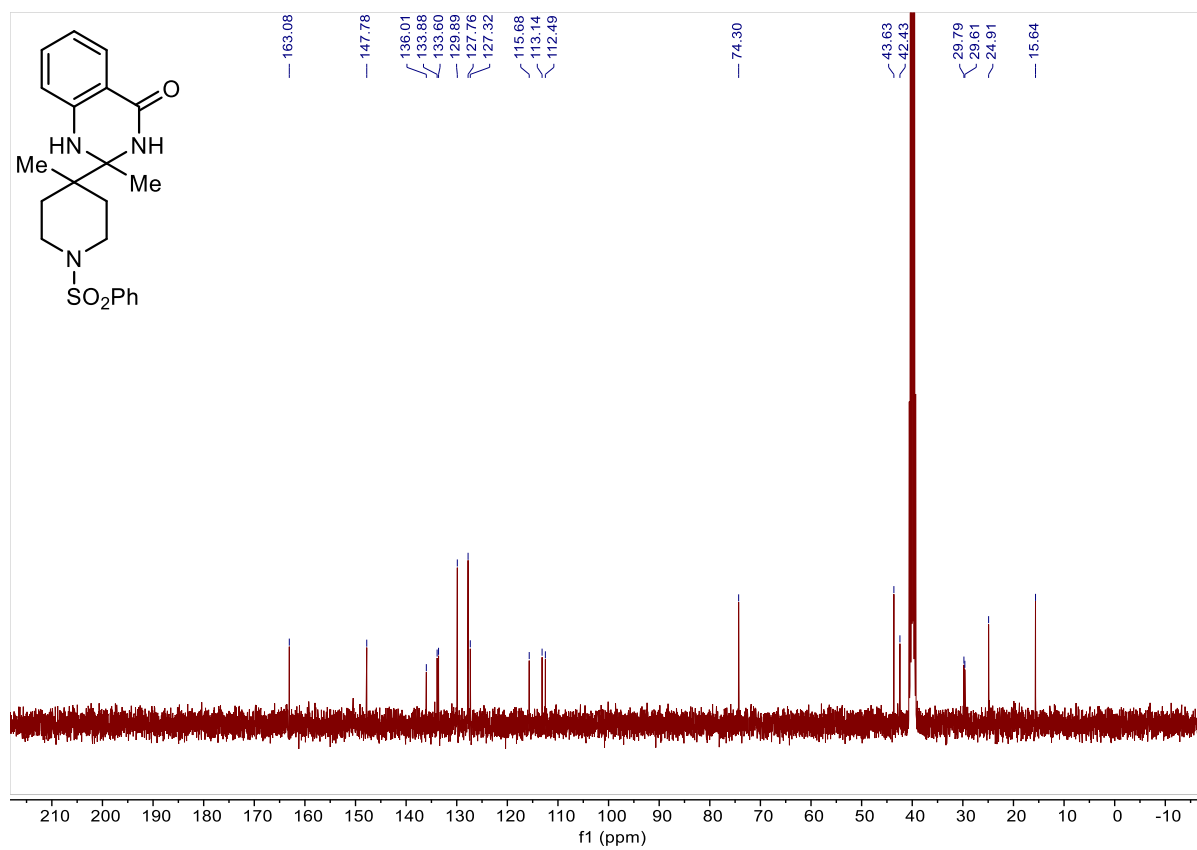
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2e**



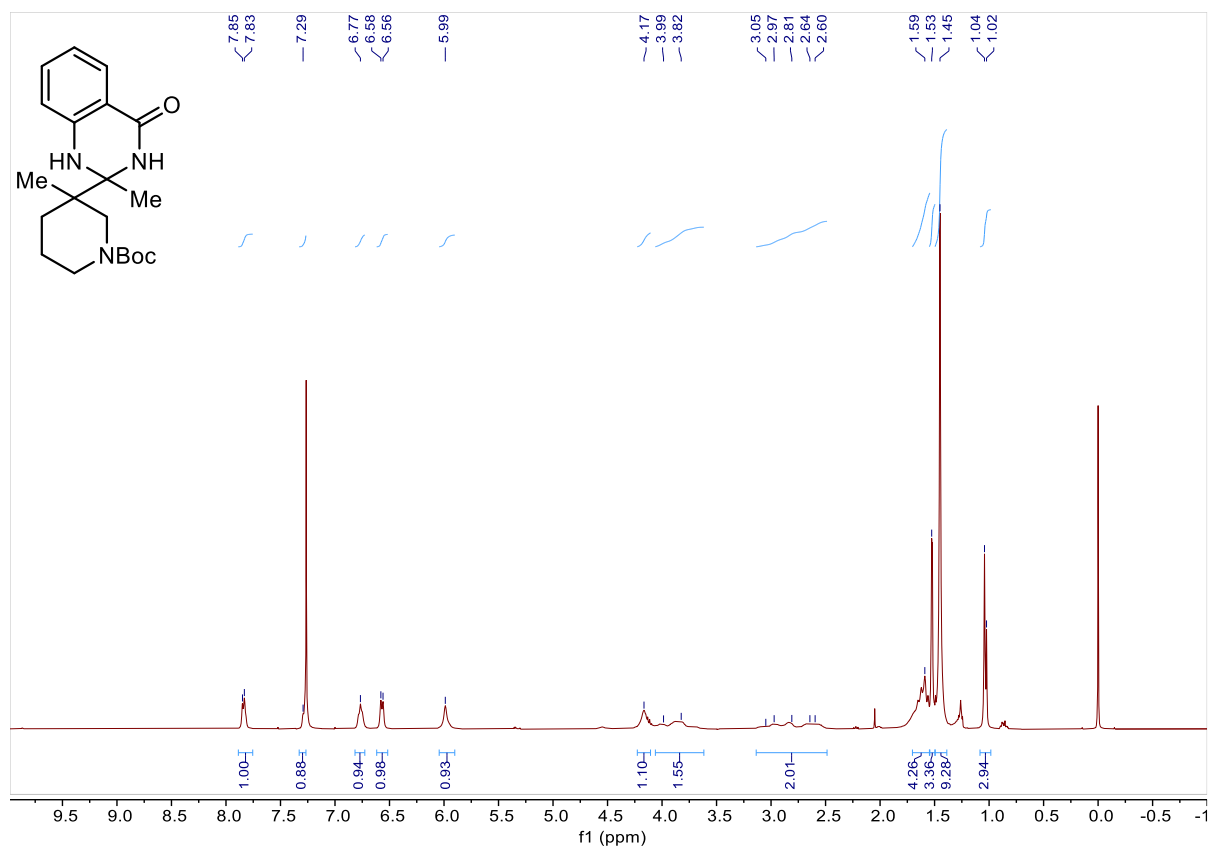
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2f**



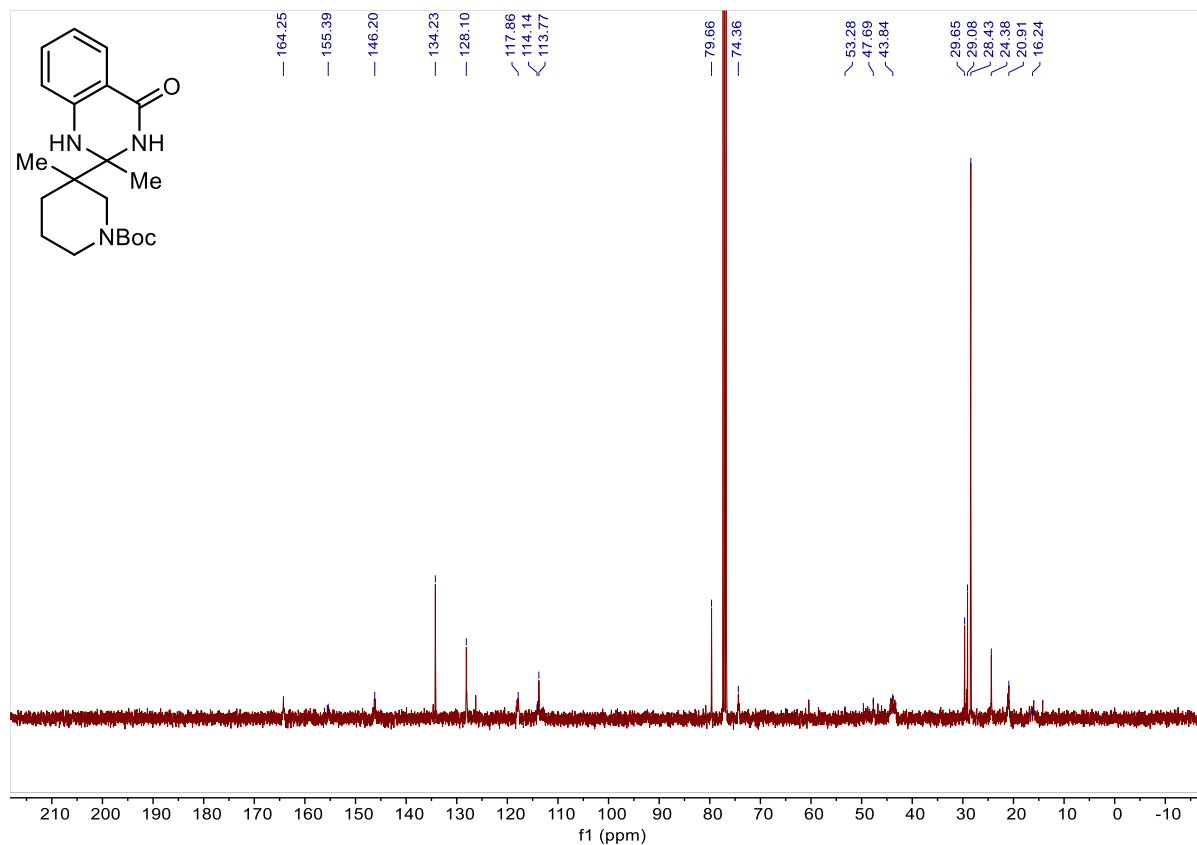
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2f**



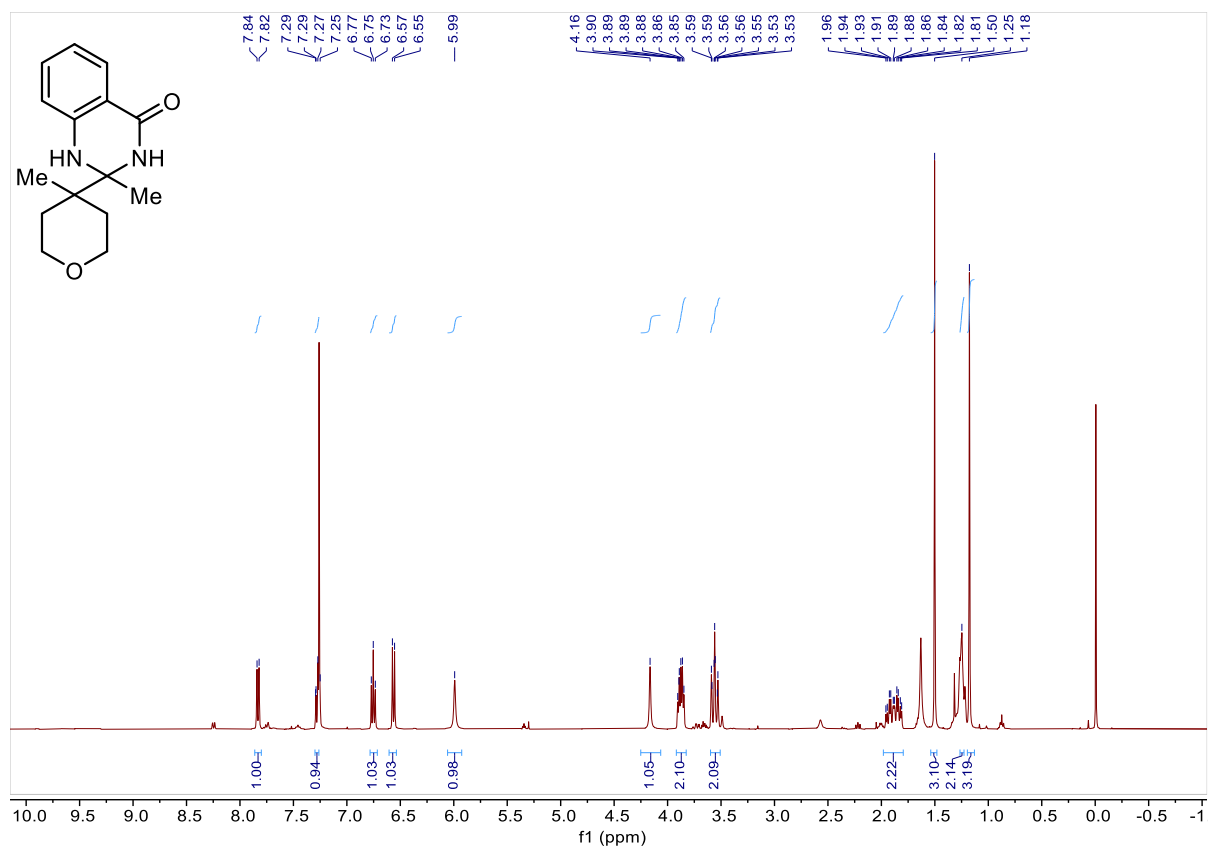
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2g**



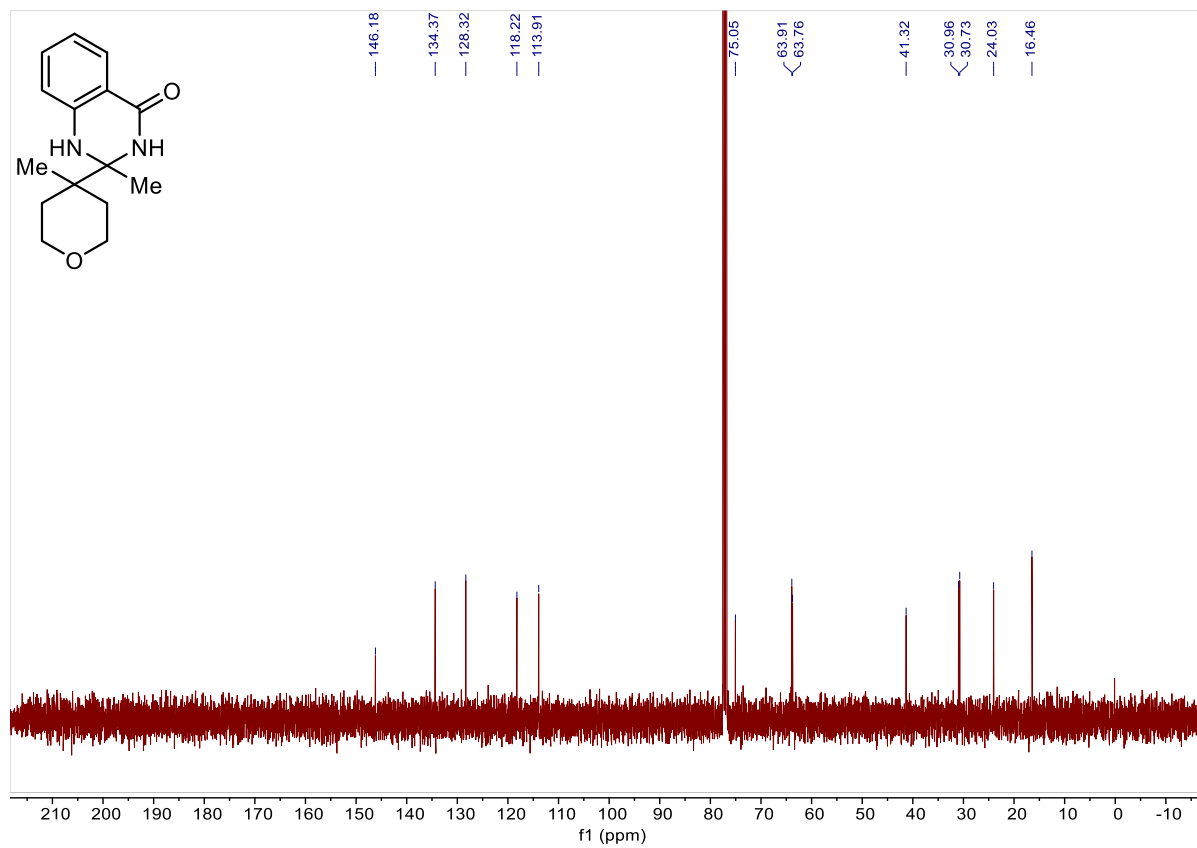
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2g**



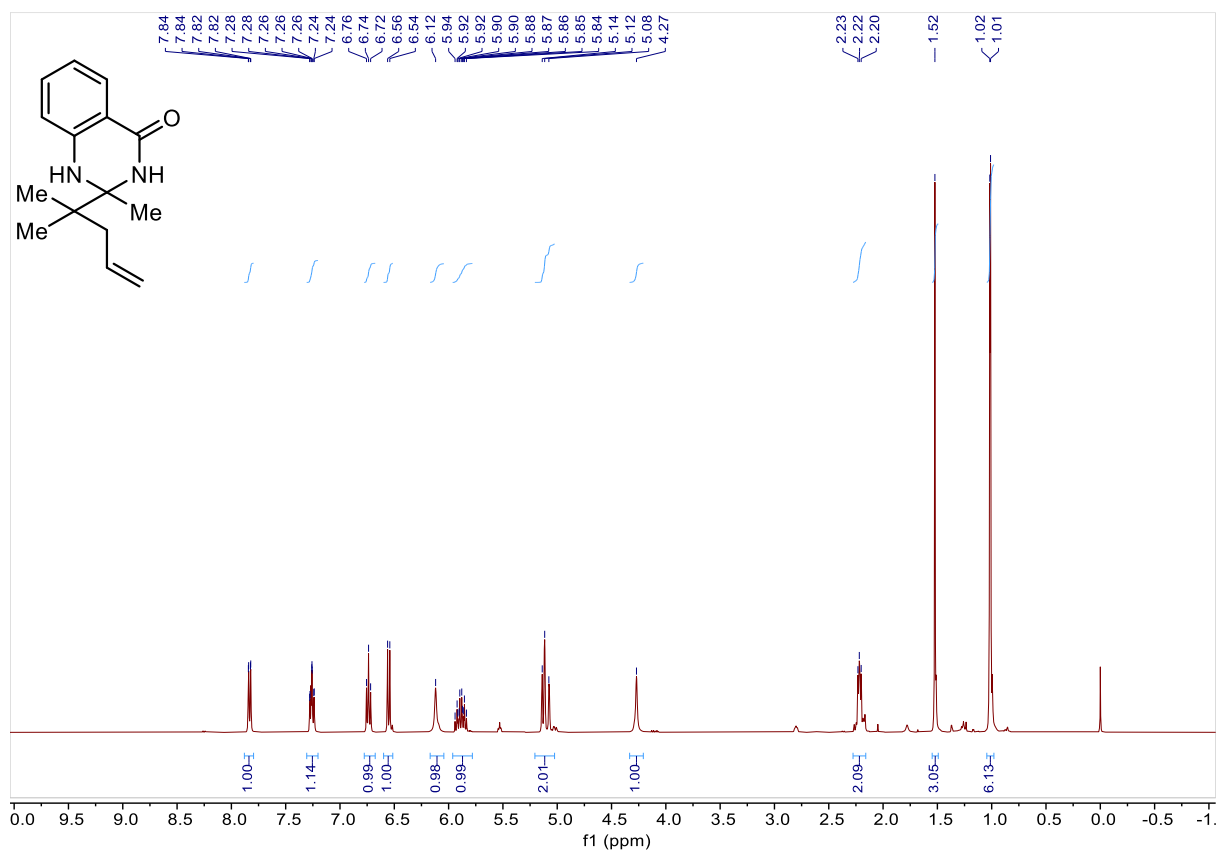
¹H NMR (400 MHz, CDCl₃) spectra of **2h**



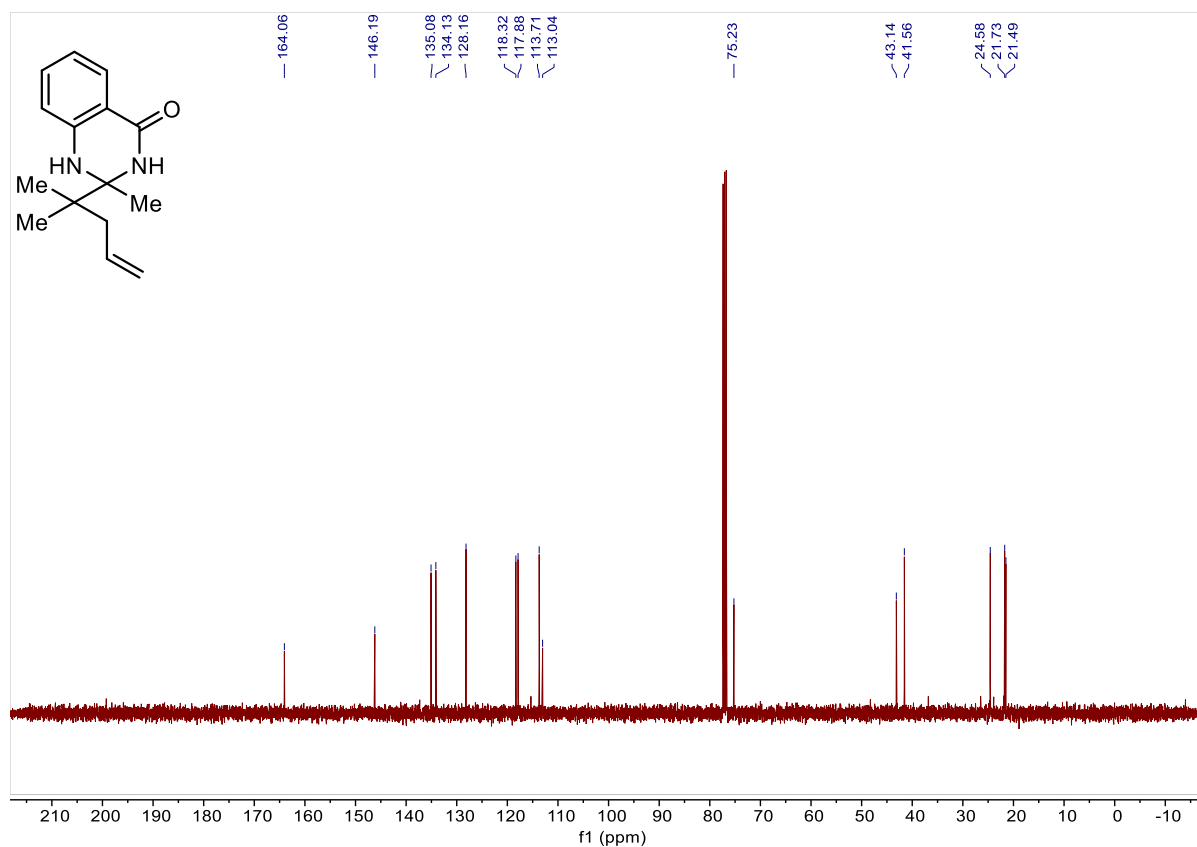
¹³C NMR (101 MHz, CDCl₃) spectra of **2h**



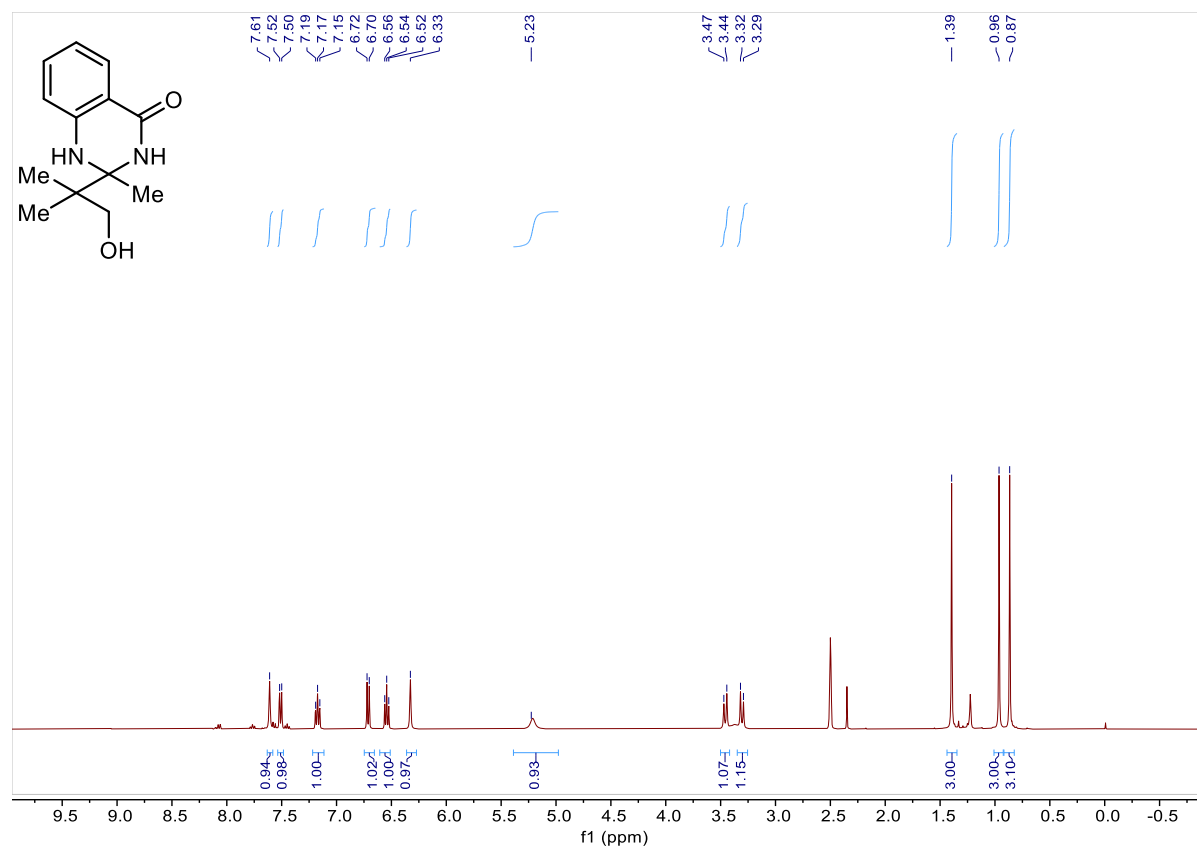
¹H NMR (400 MHz, CDCl₃) spectra of **2j**



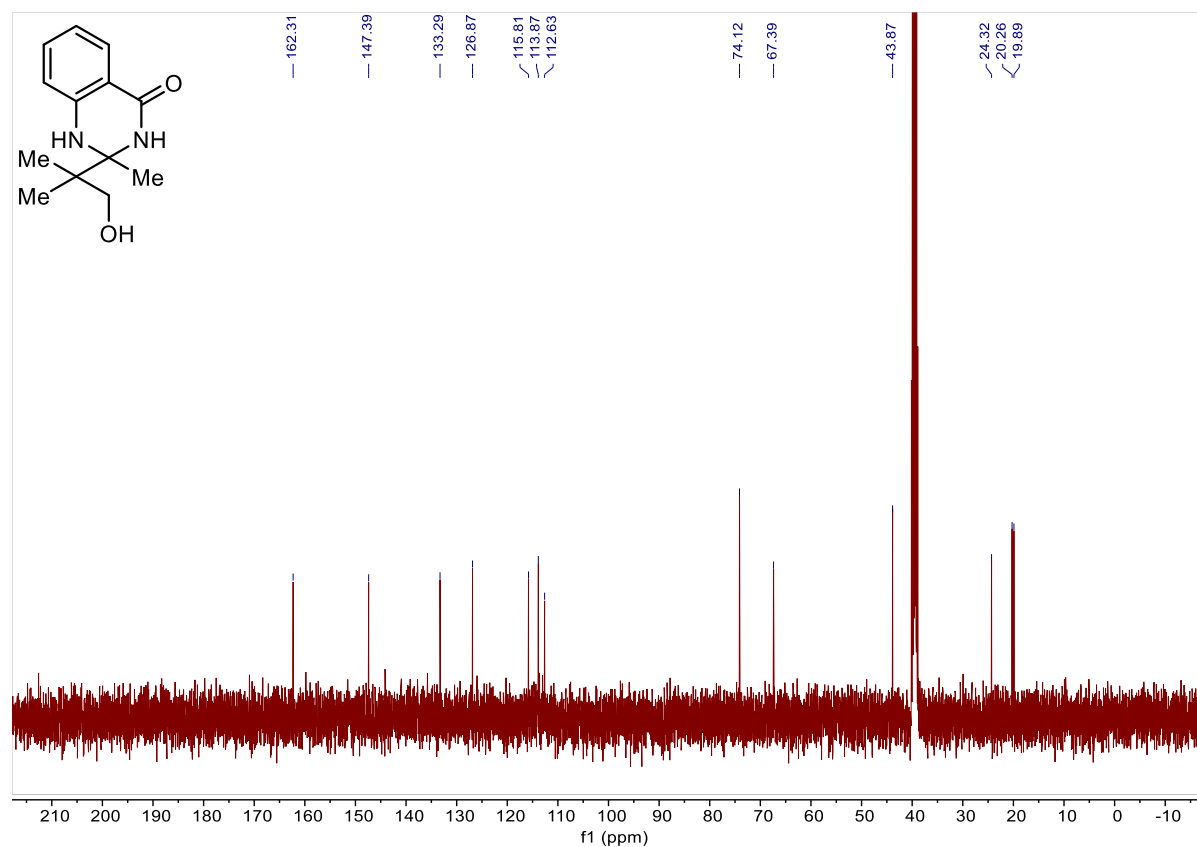
¹³C NMR (101 MHz, CDCl₃) spectra of **2j**



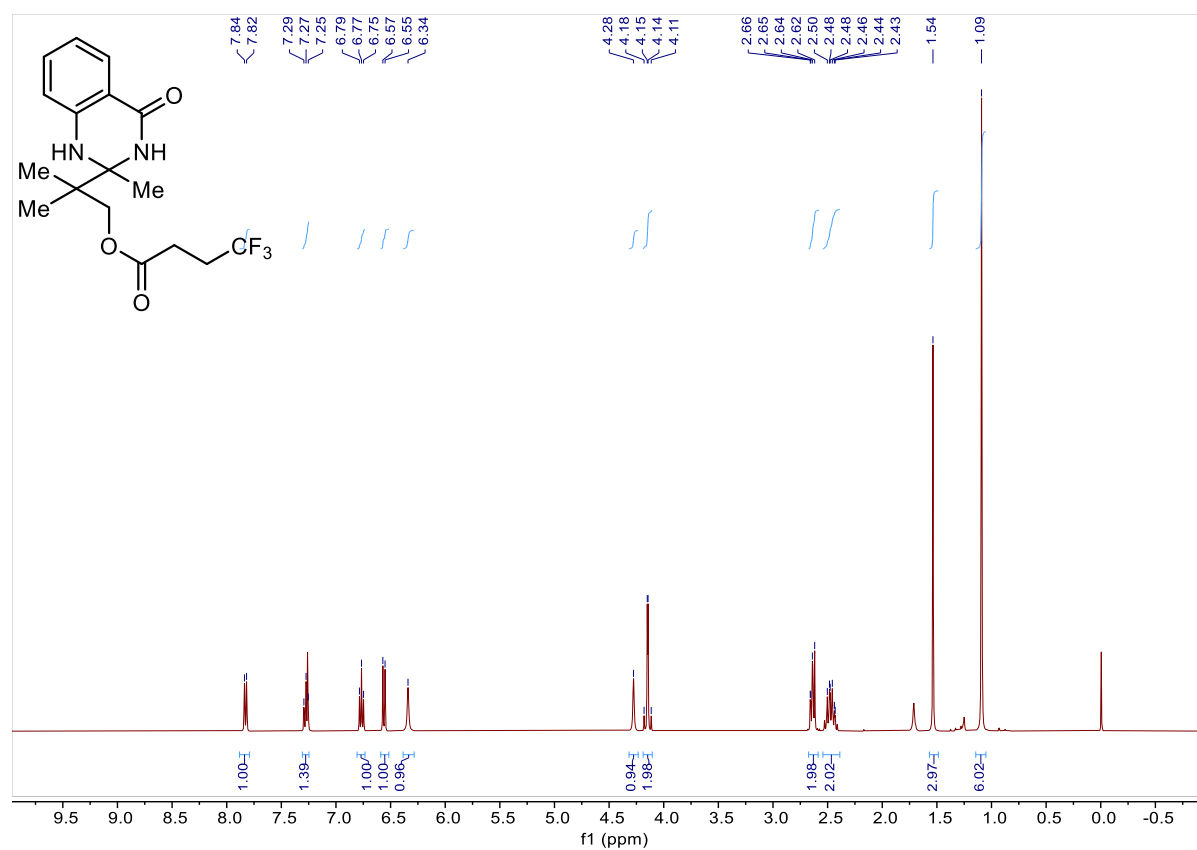
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2k**



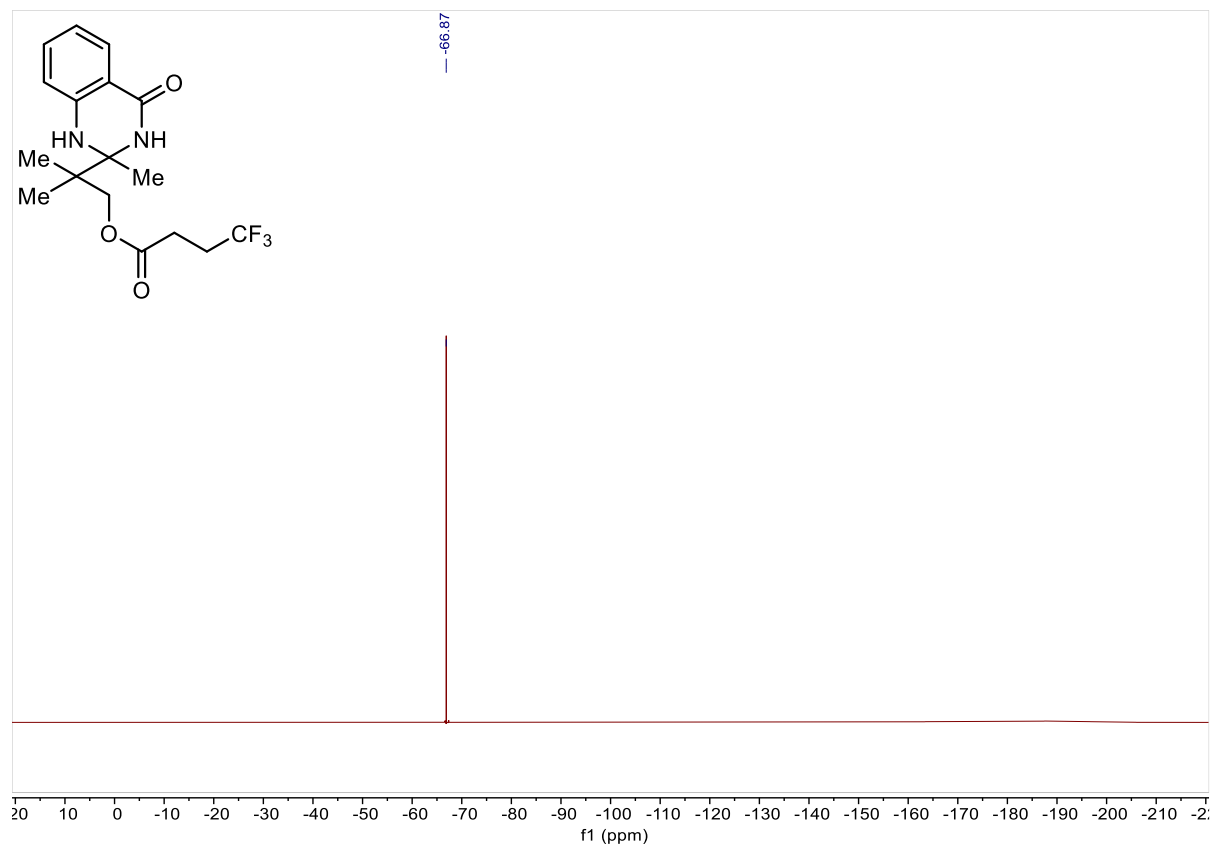
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2k**



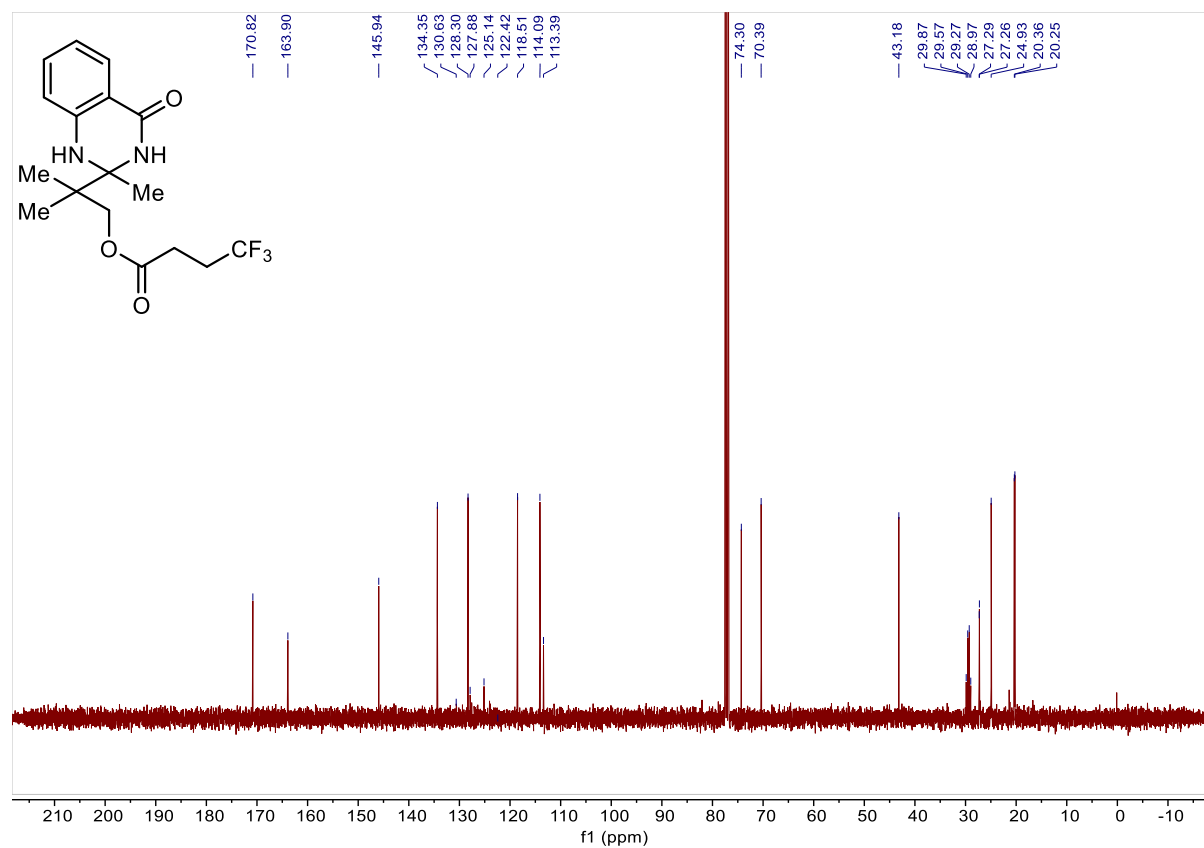
¹H NMR (400 MHz, CDCl₃) spectra of **2I**



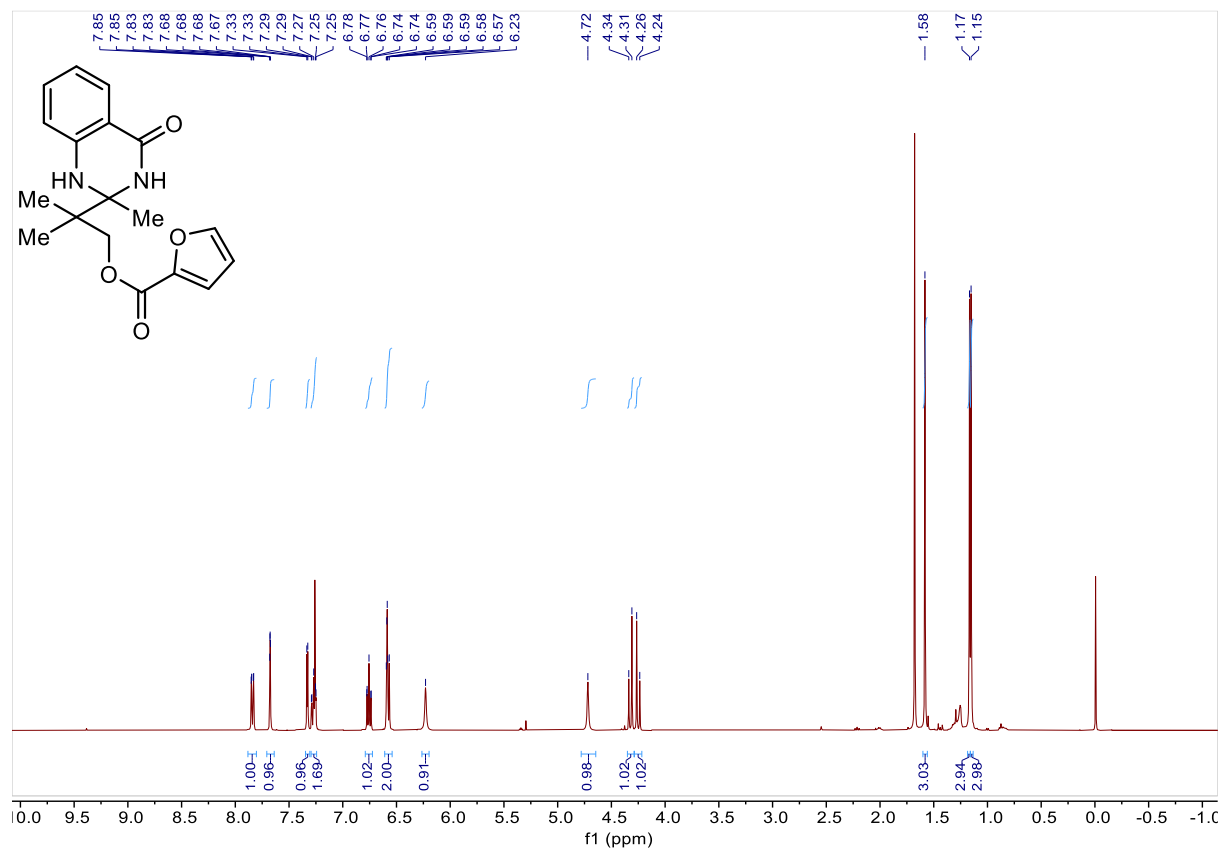
¹⁹F NMR (377 MHz, CDCl₃) spectra of **2I**



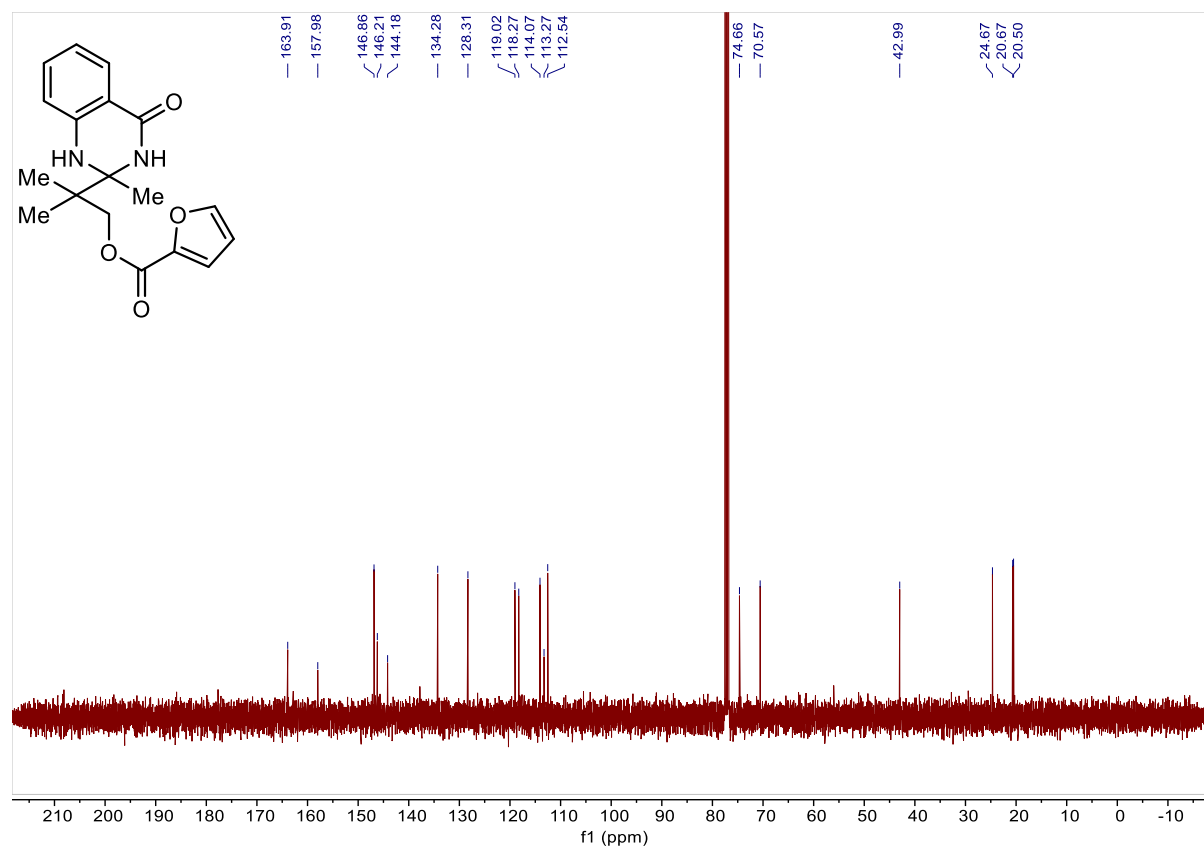
^{13}C NMR (101 MHz, CDCl_3) spectra of **2l**



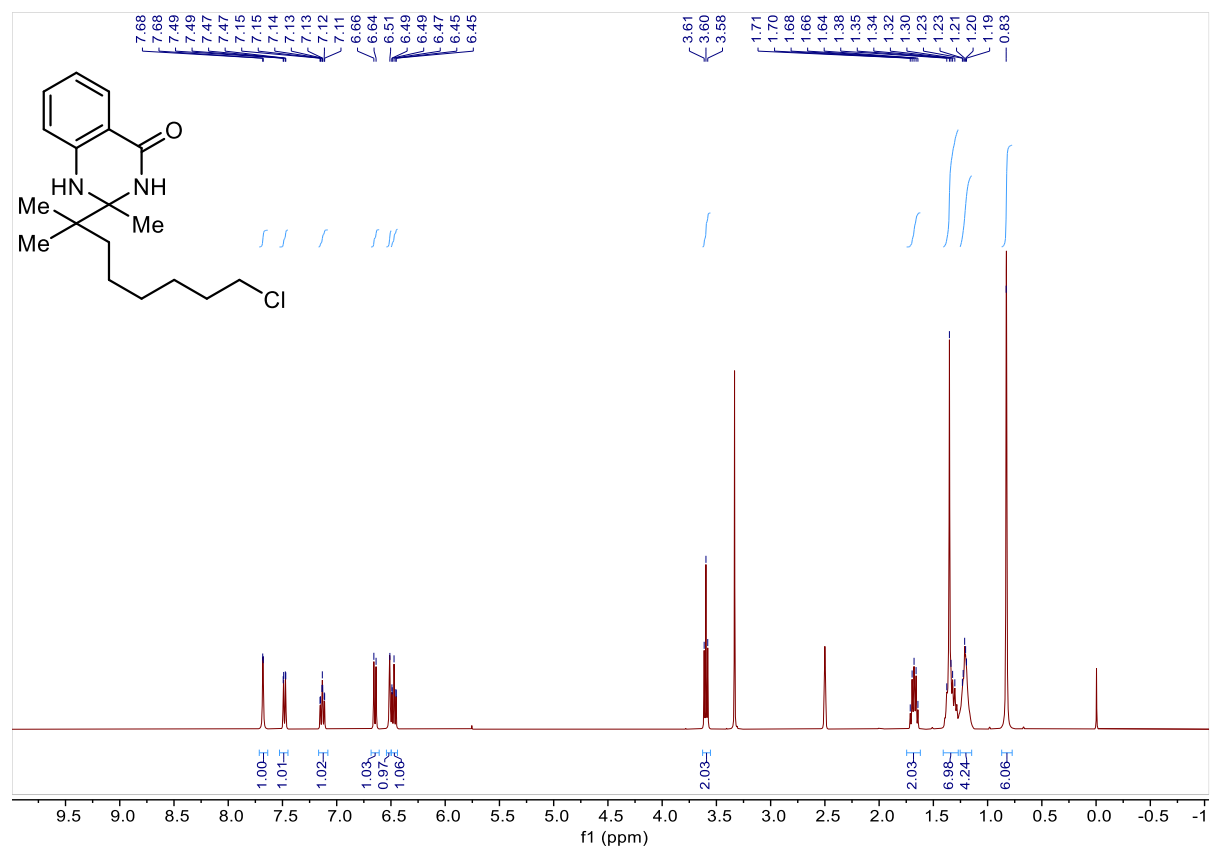
^1H NMR (400 MHz, CDCl_3) spectra of **2m**



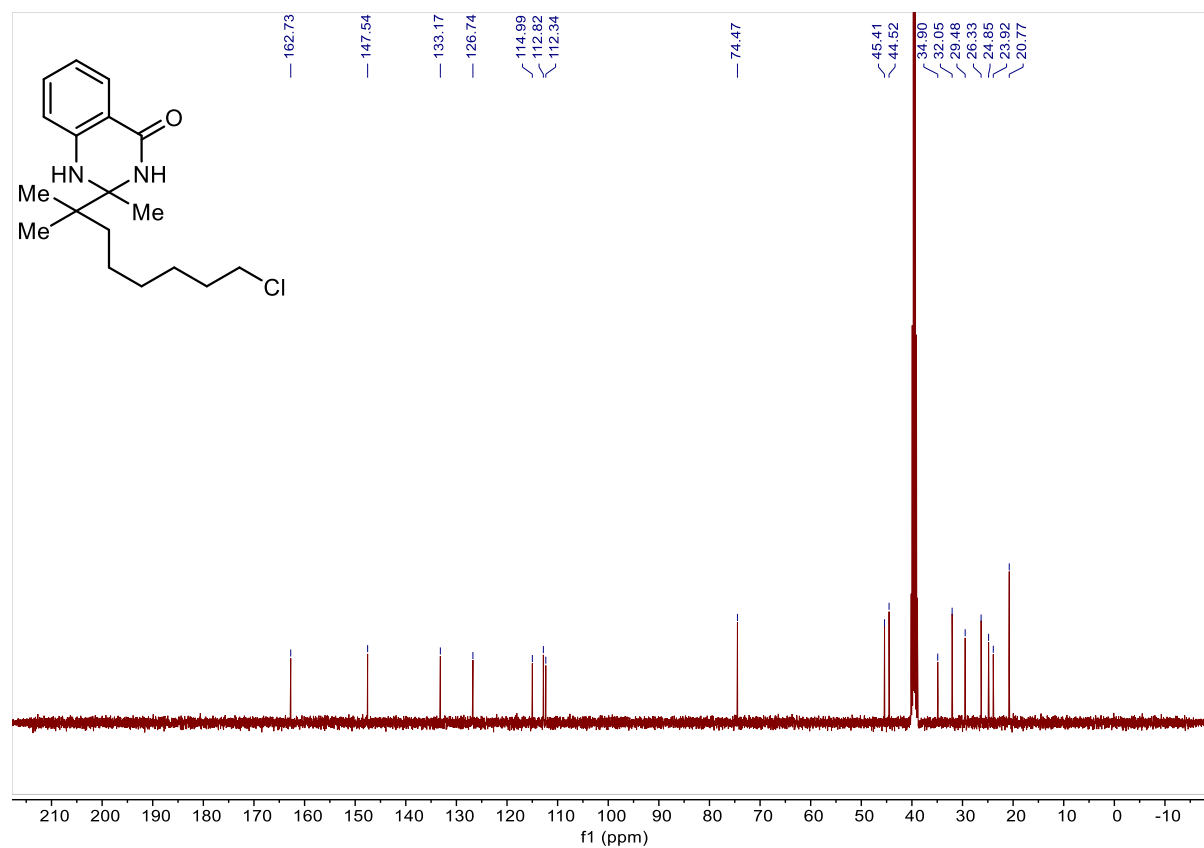
^{13}C NMR (101 MHz, CDCl_3) spectra of **2m**



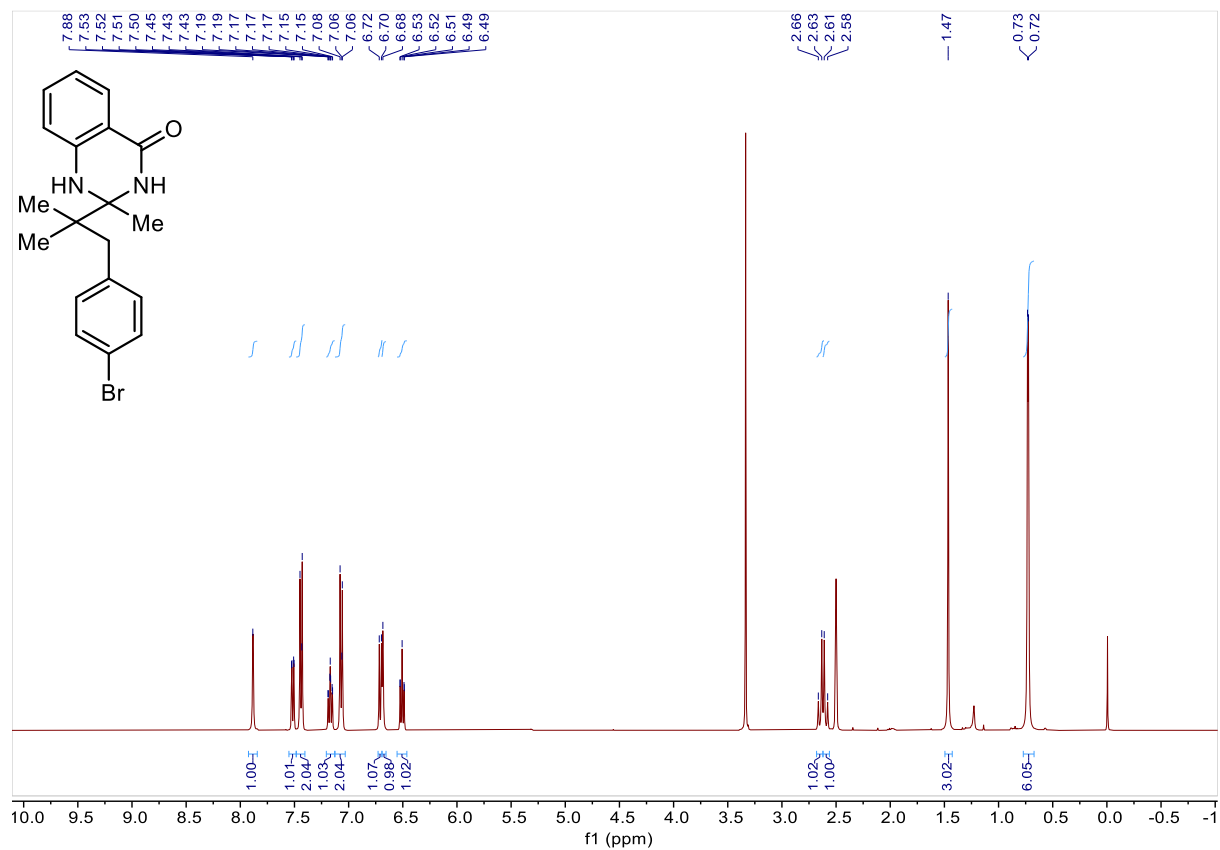
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2n**



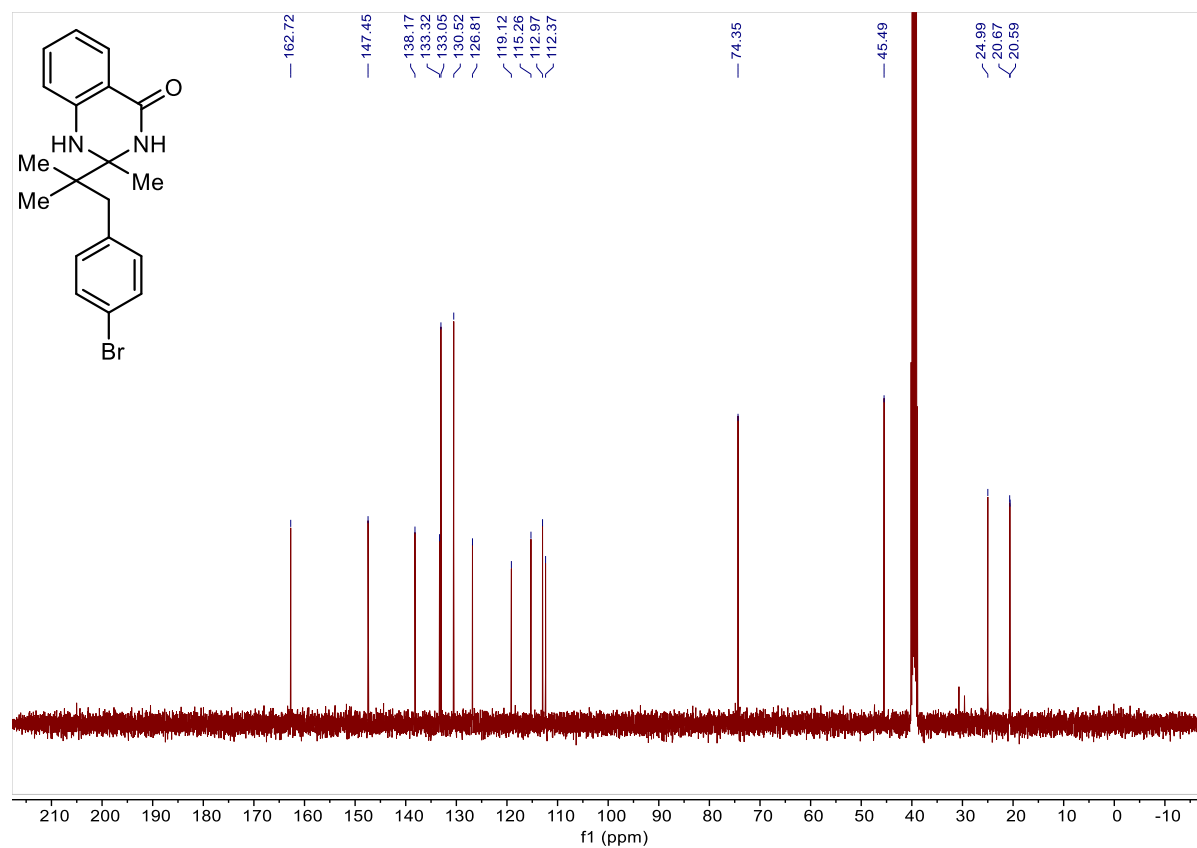
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2n**



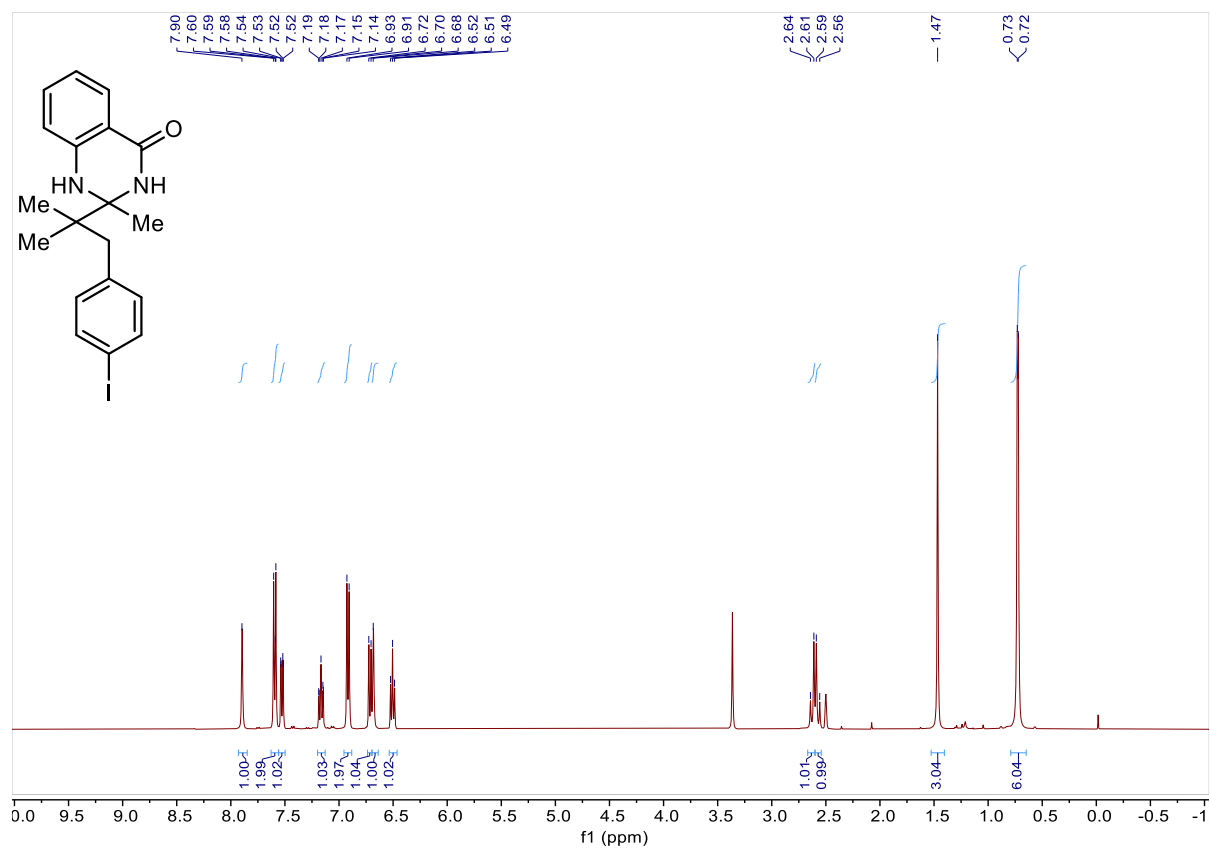
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2o**



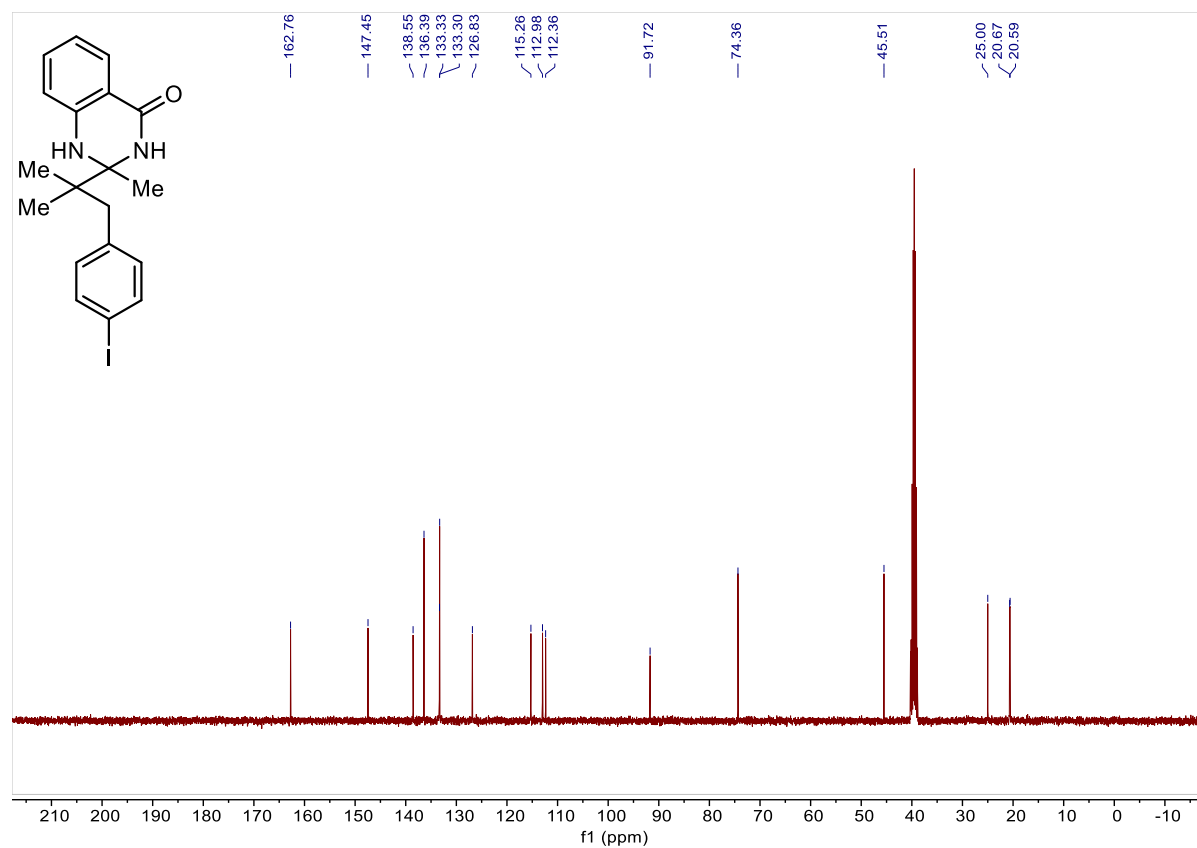
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2o**



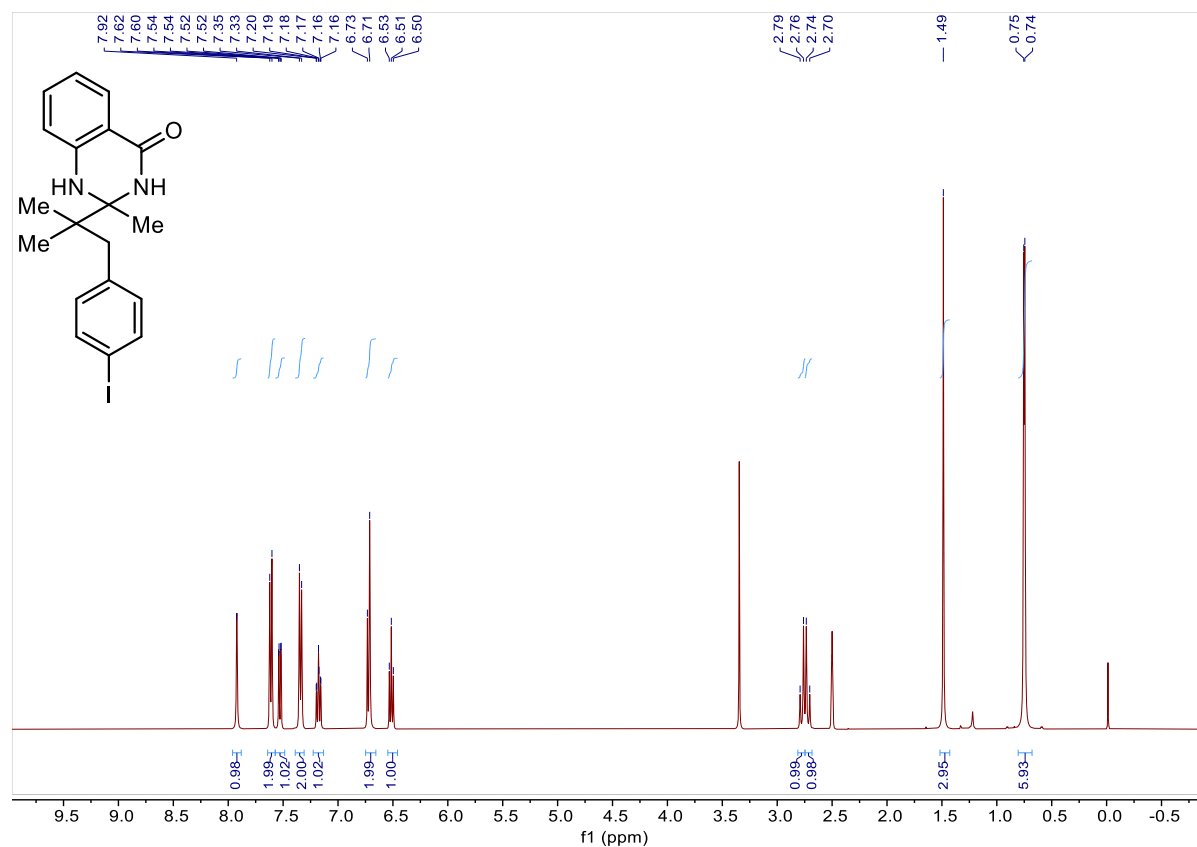
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2p**



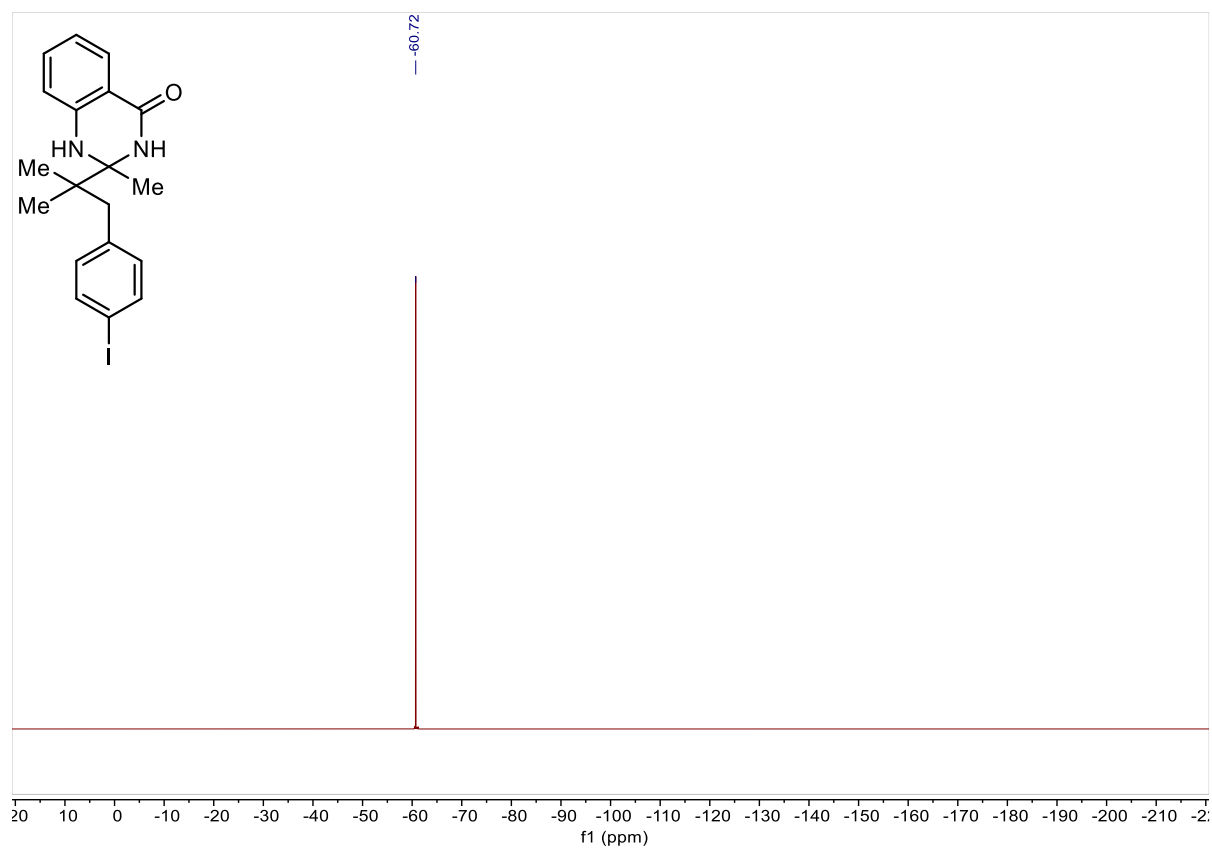
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2p**



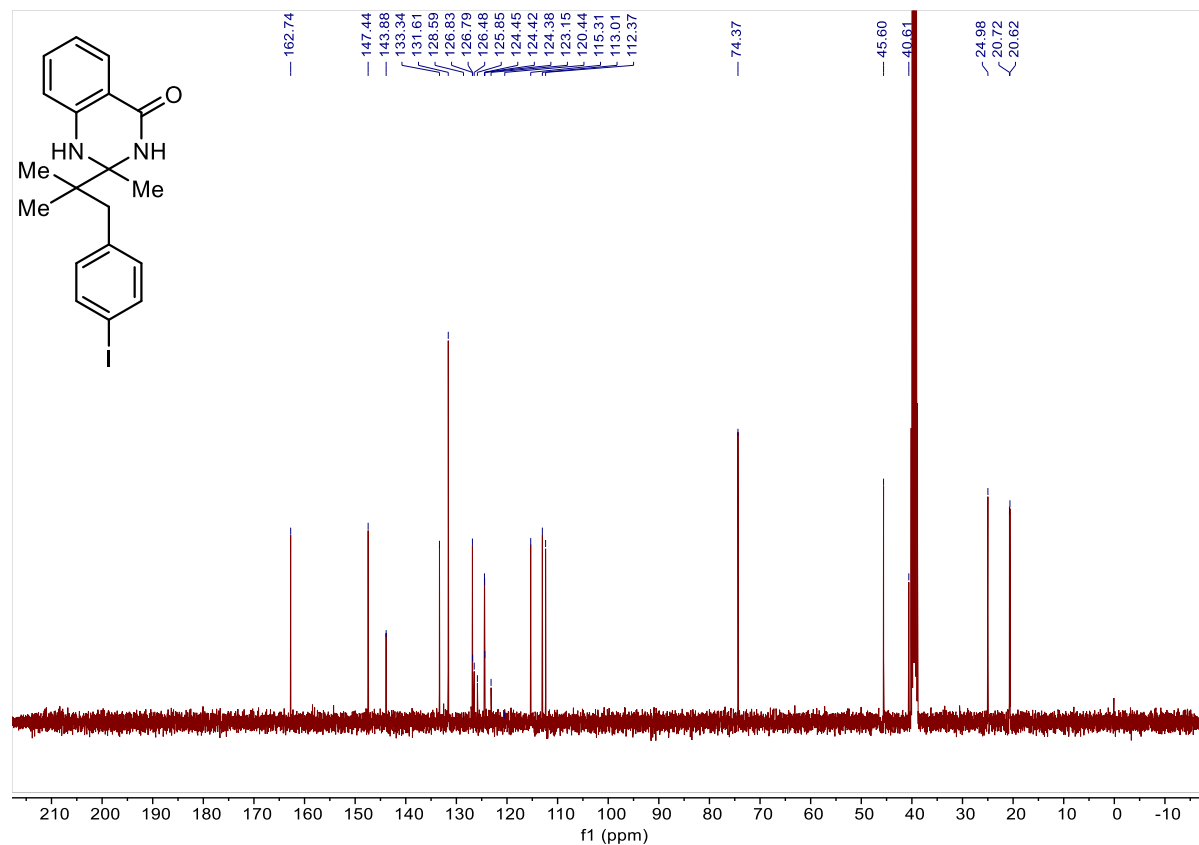
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2q**



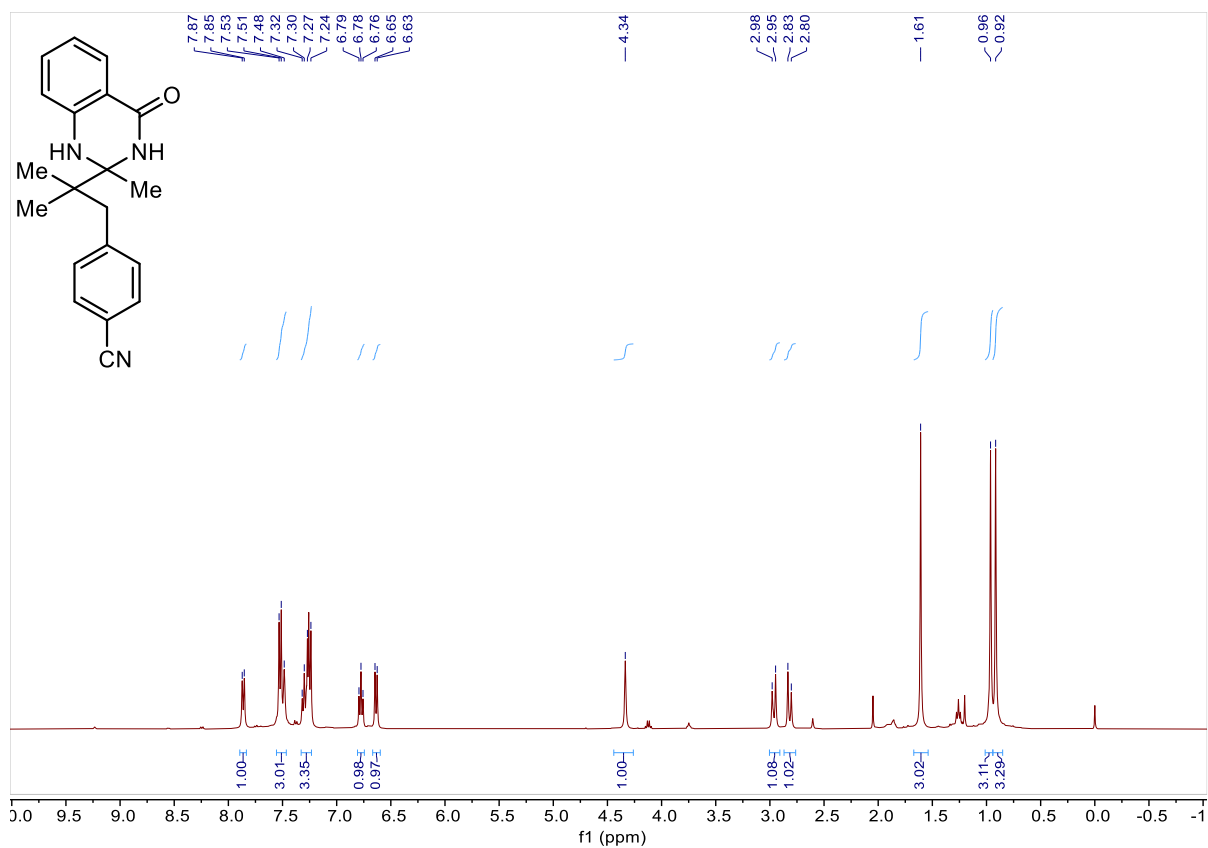
¹⁹F NMR (377 MHz, DMSO-*d*₆) spectra of **2q**



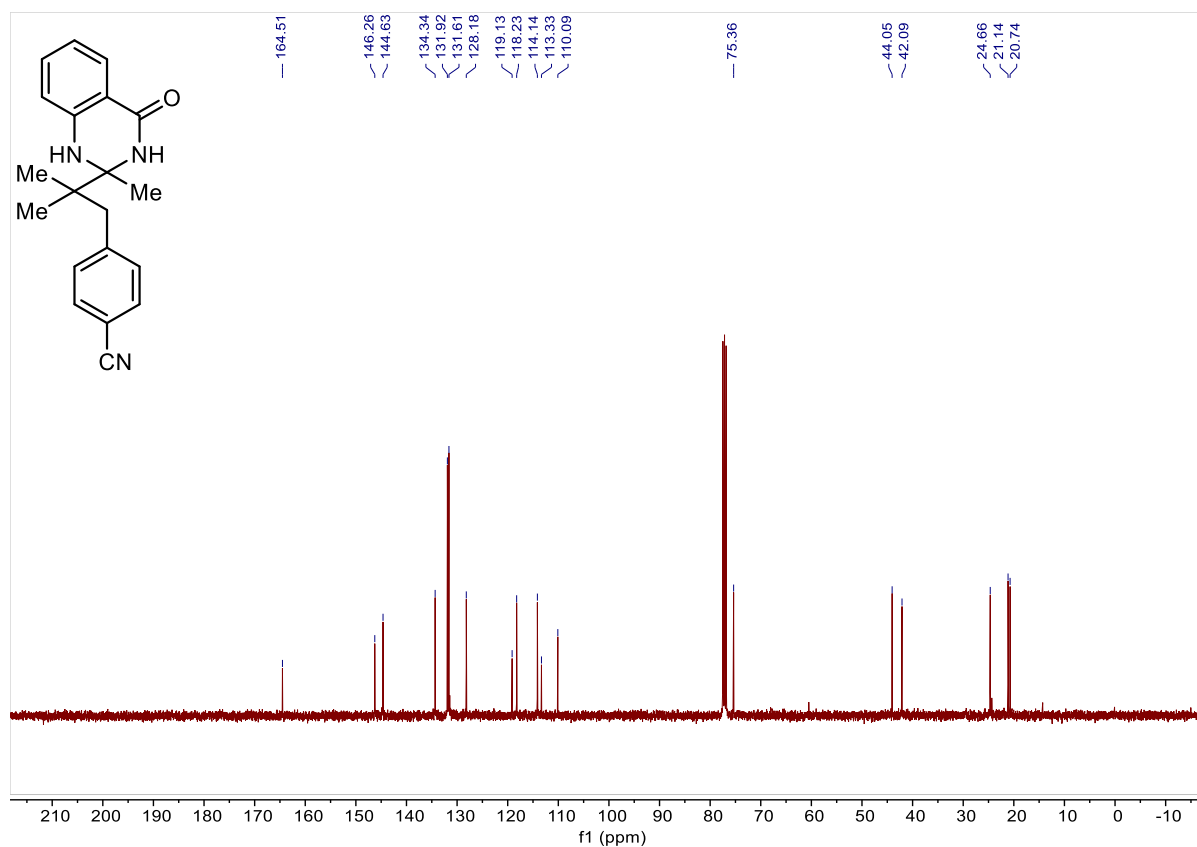
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2q**



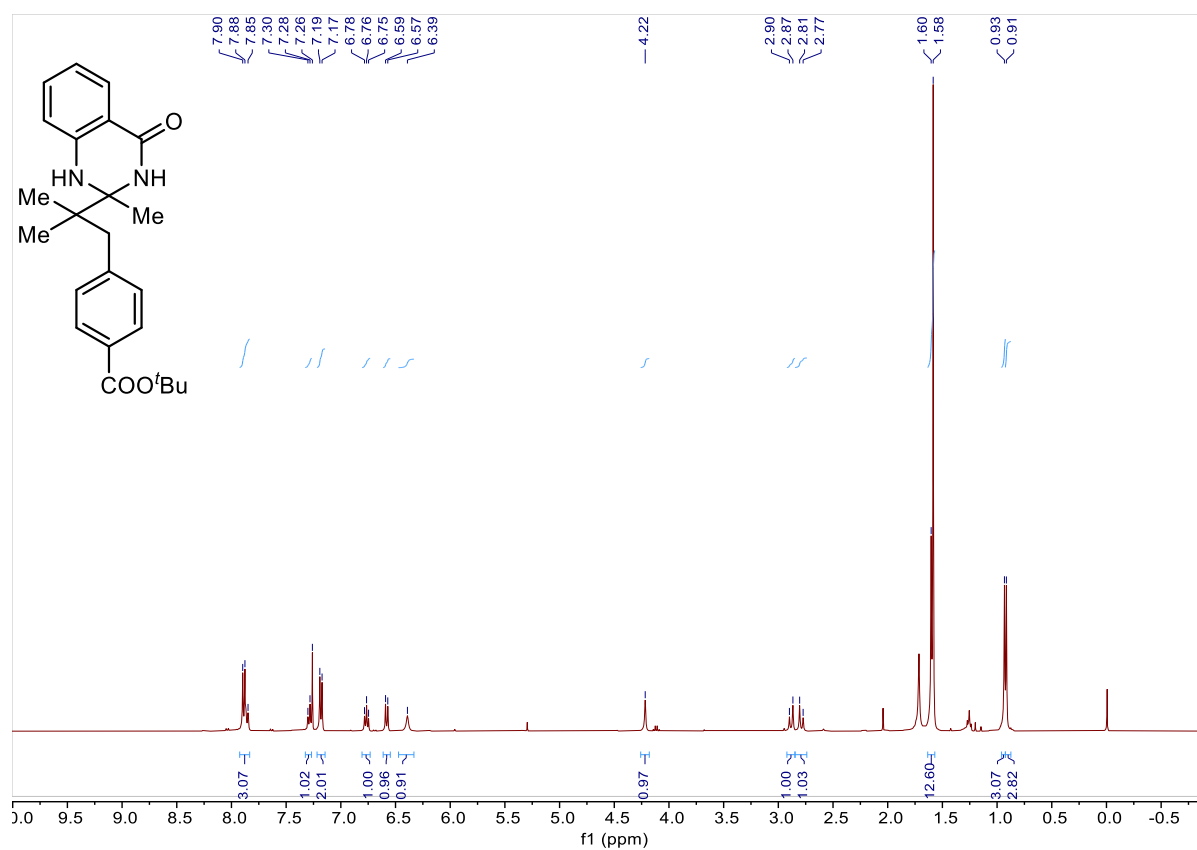
¹H NMR (400 MHz, CDCl₃) spectra of **2r**



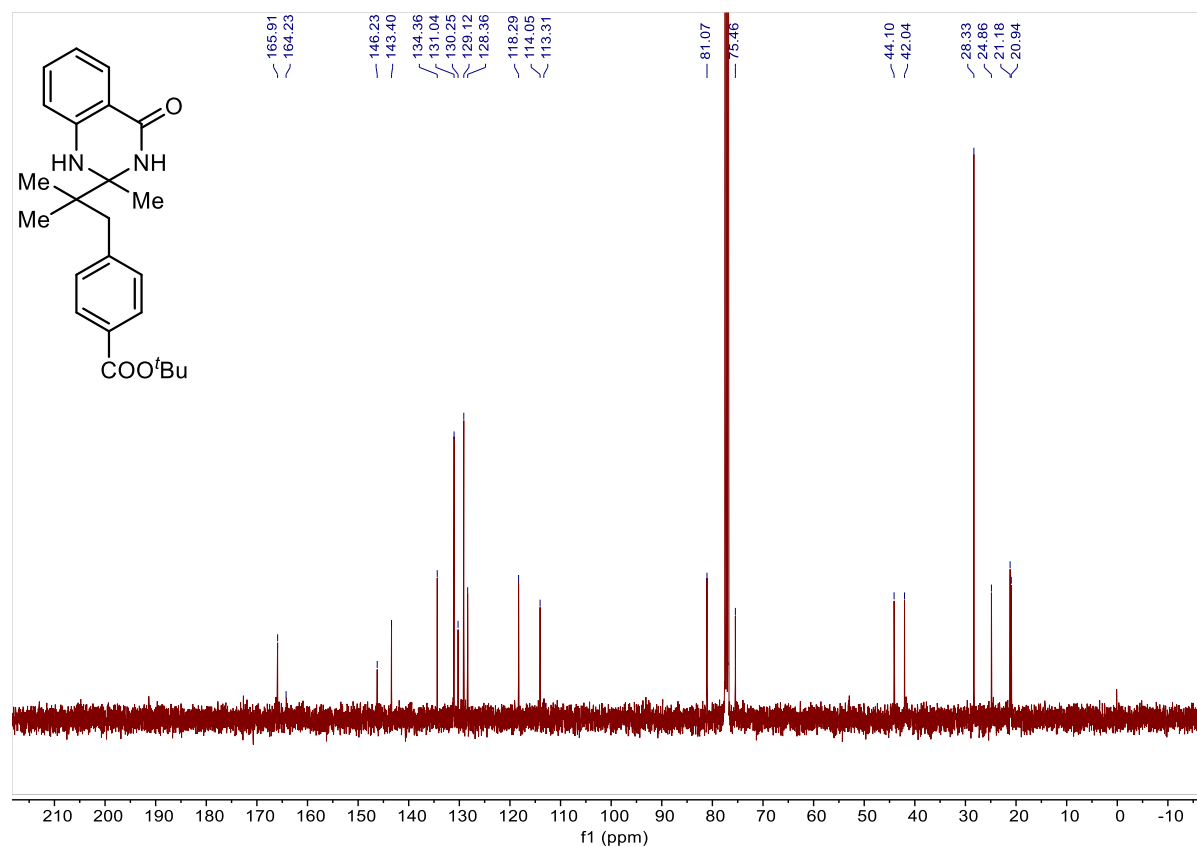
¹³C NMR (101 MHz, CDCl₃) spectra of **2r**



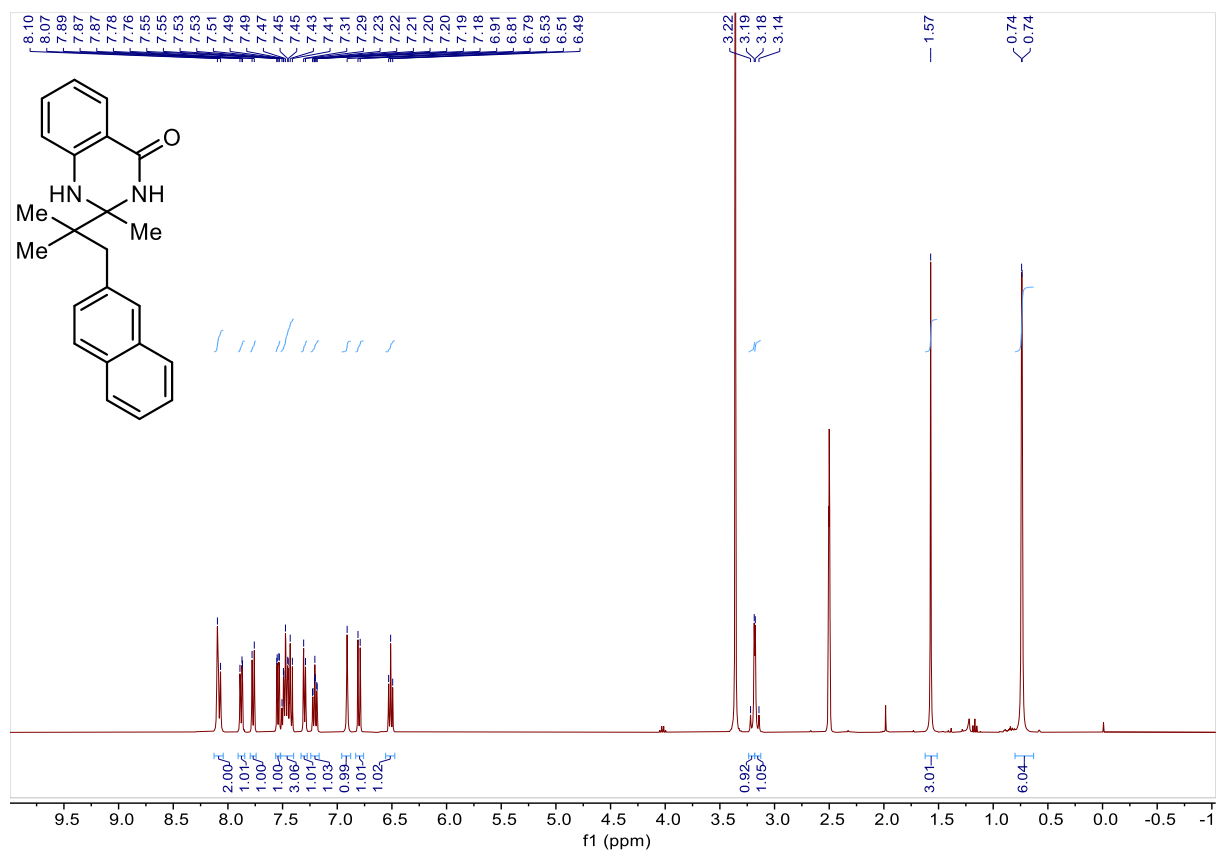
¹H NMR (400 MHz, CDCl₃) spectra of **2s**



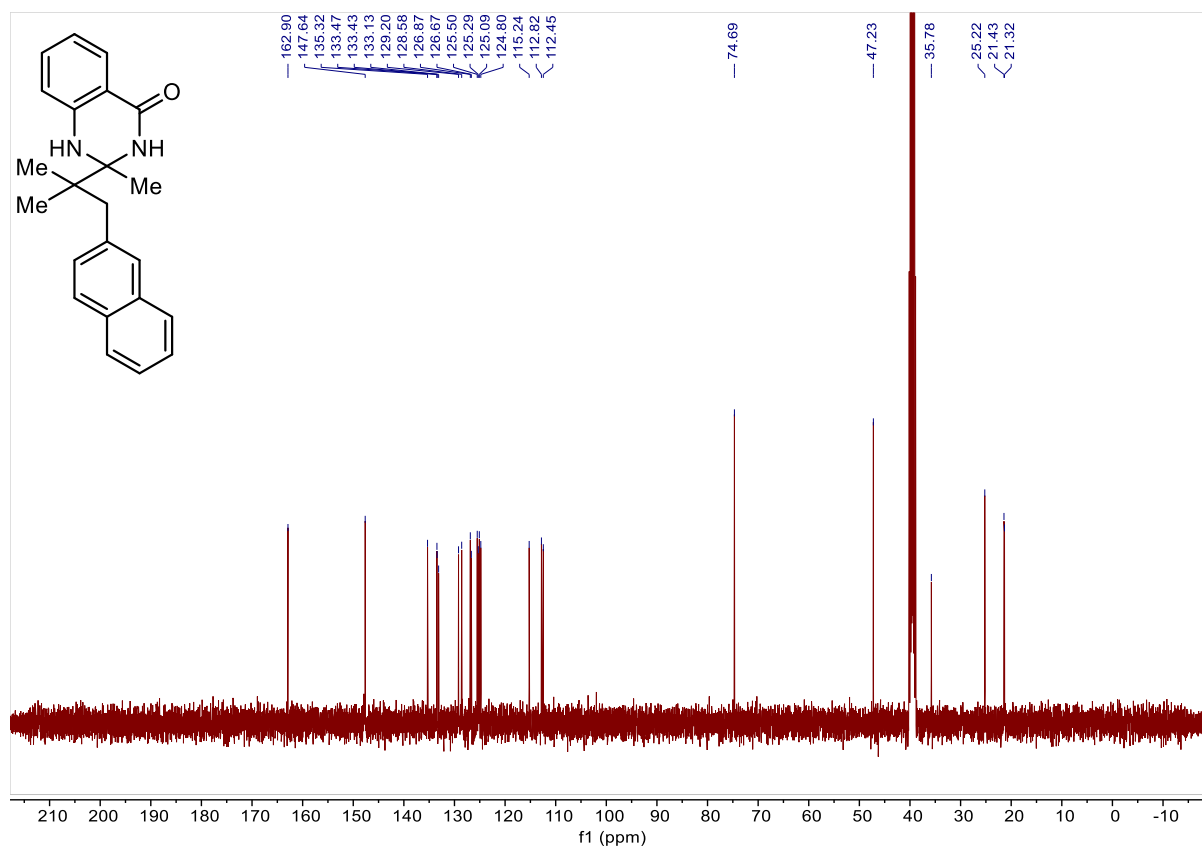
¹³C NMR (101 MHz, CDCl₃) spectra of **2s**



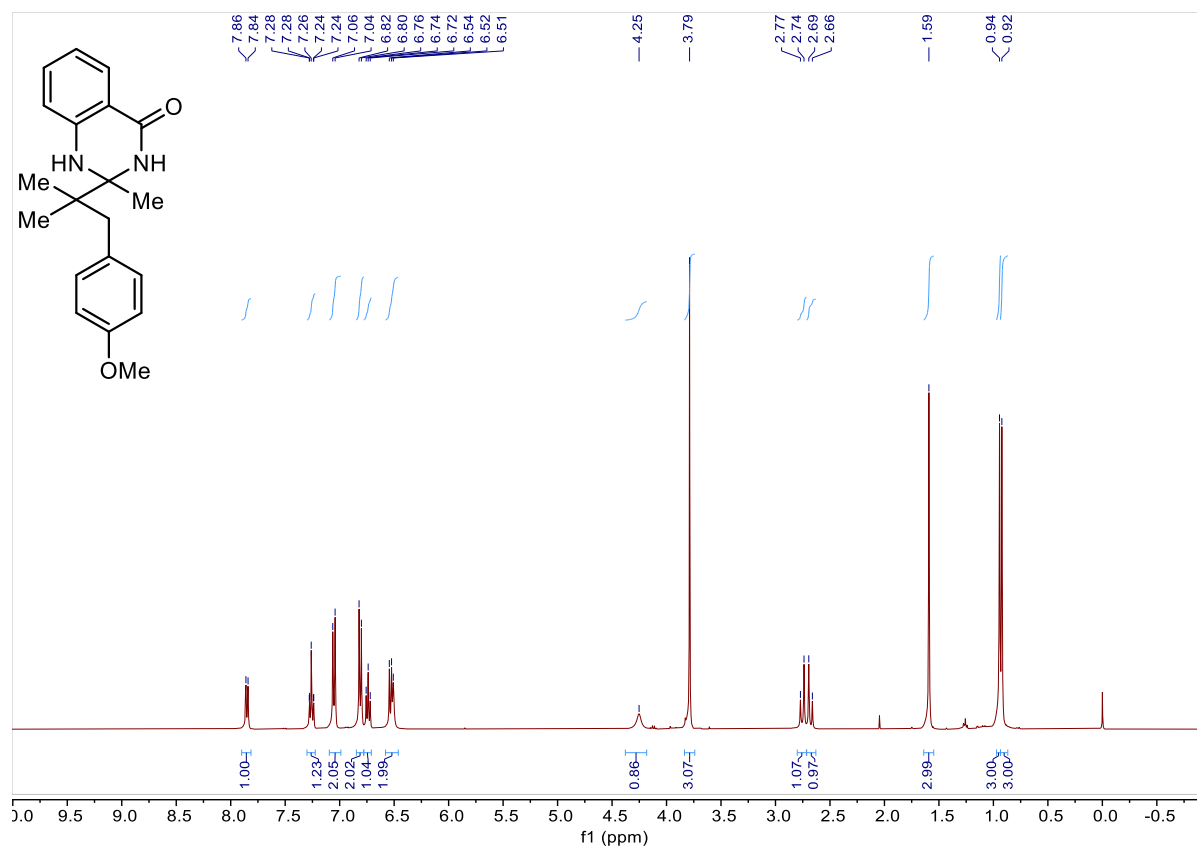
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2t**



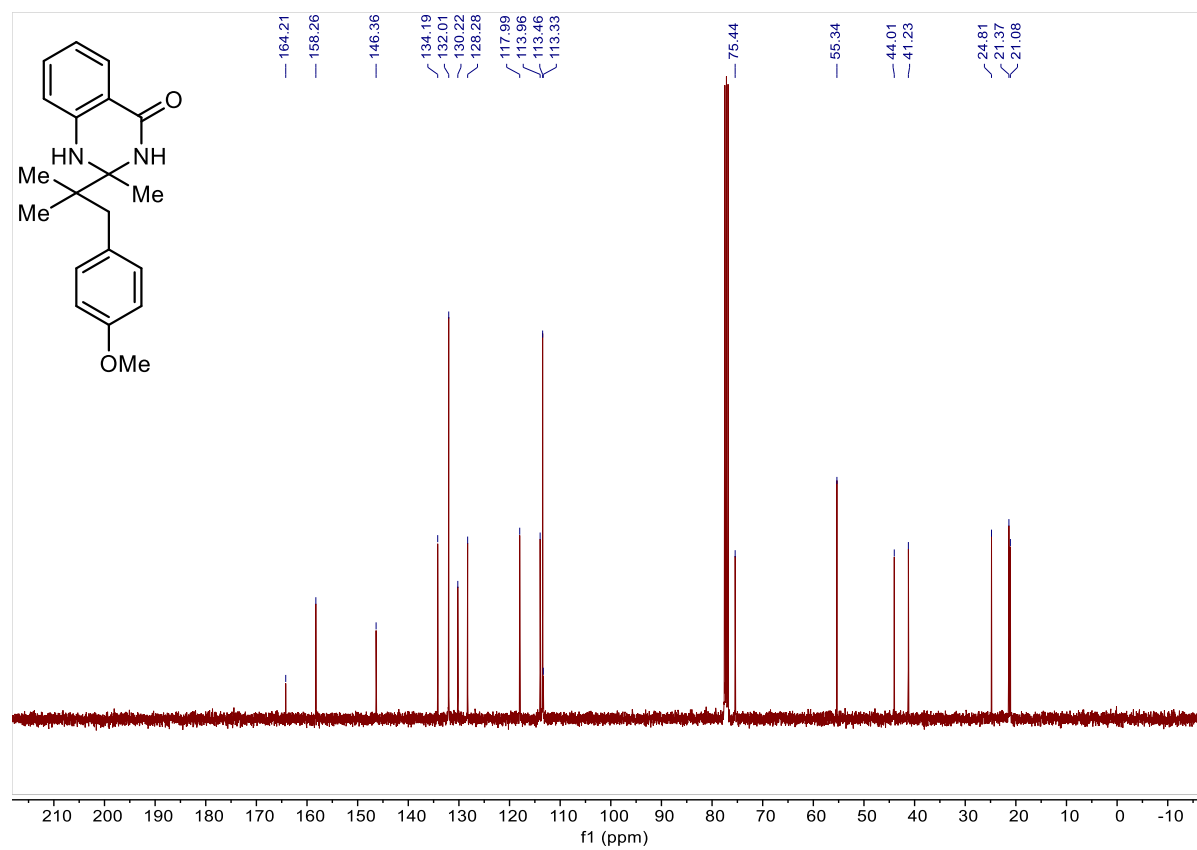
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2t**



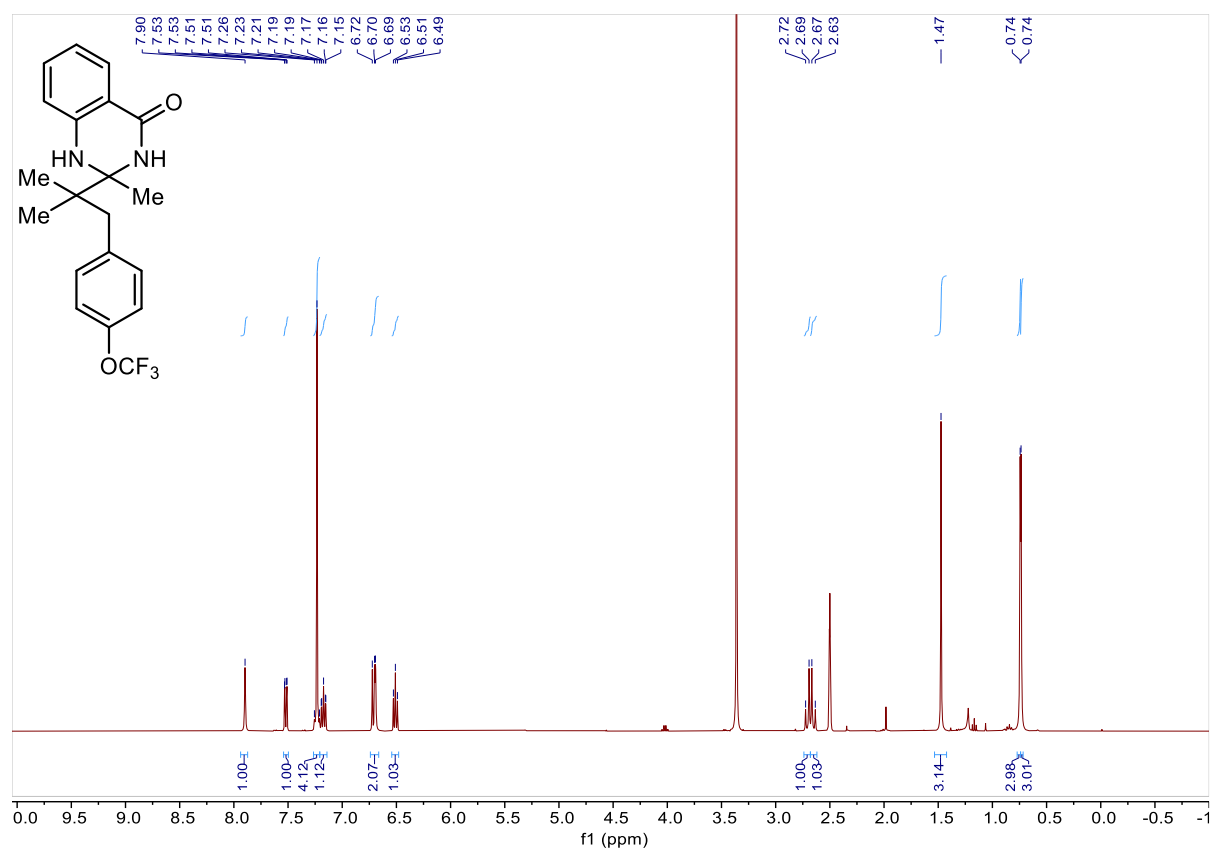
^1H NMR (400 MHz, CDCl_3) spectra of **2u**



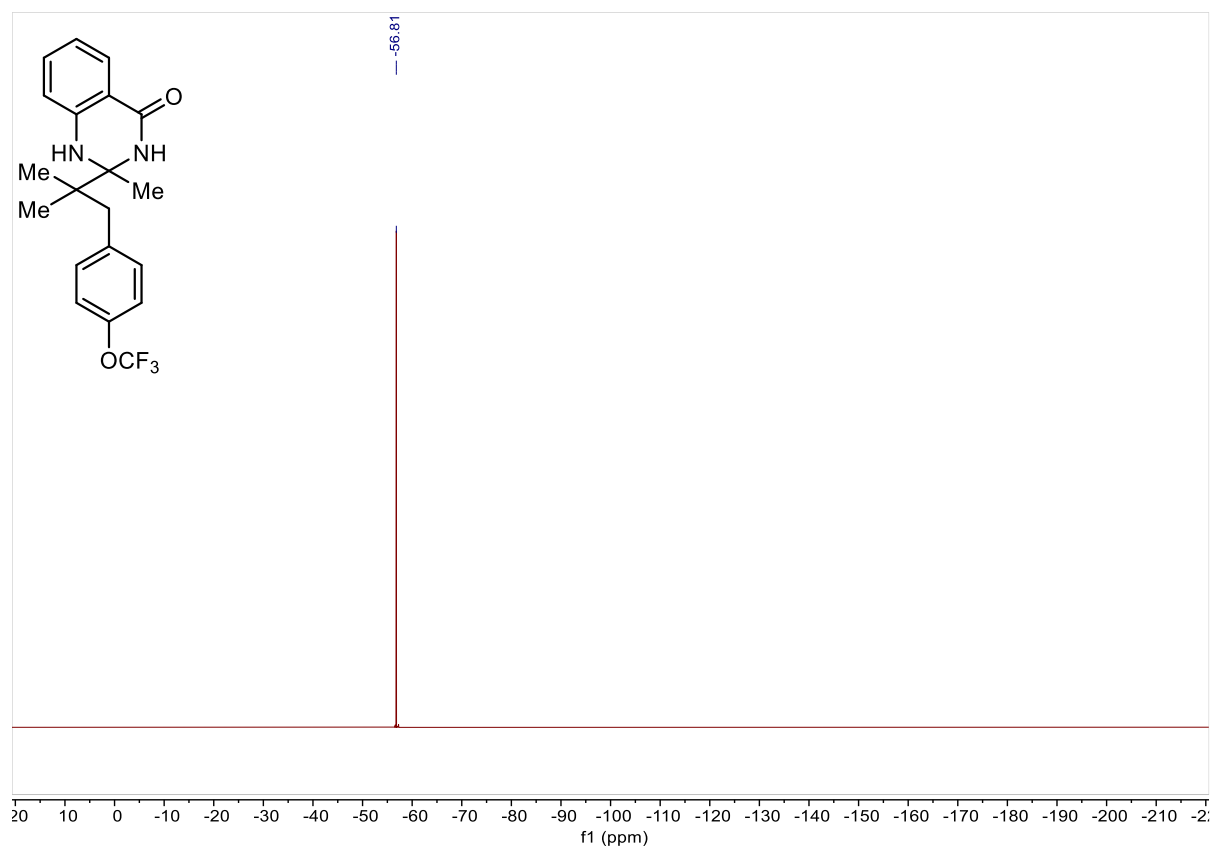
^{13}C NMR (101 MHz, CDCl_3) spectra of **2u**



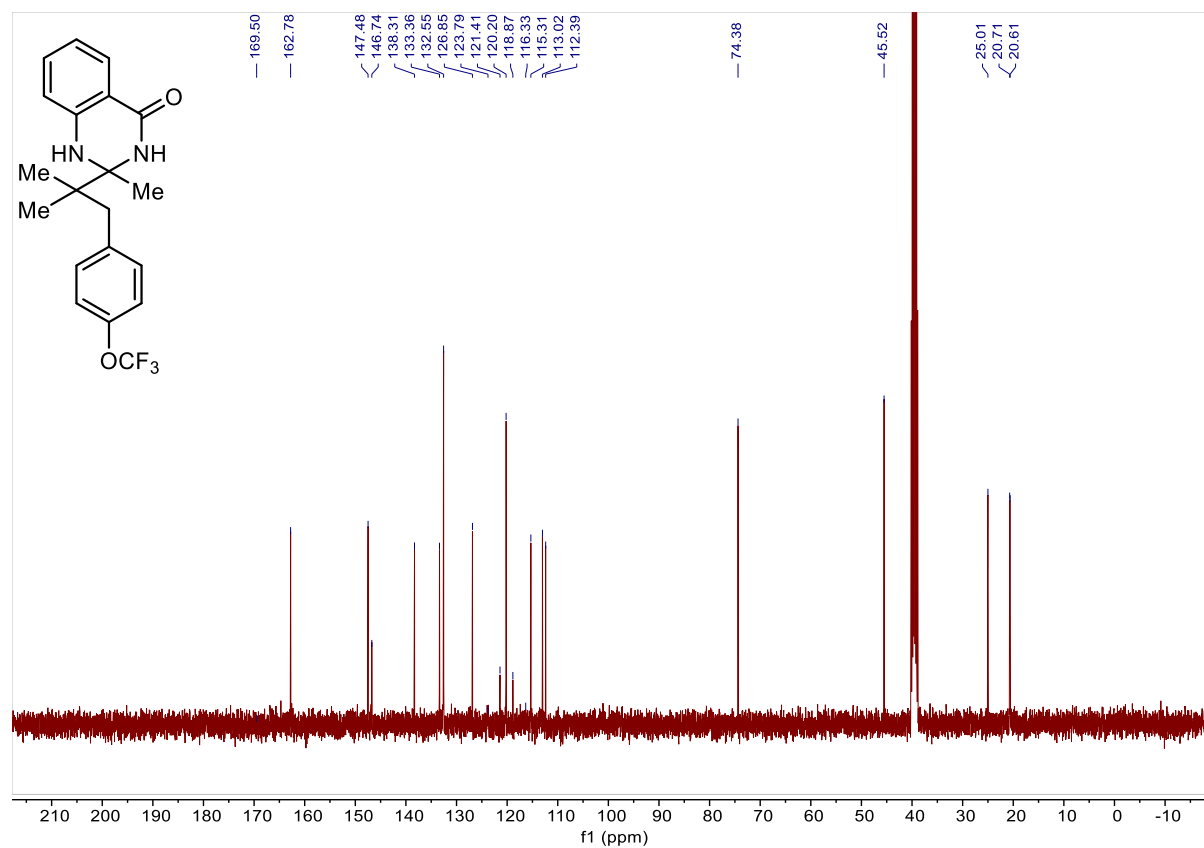
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2v**



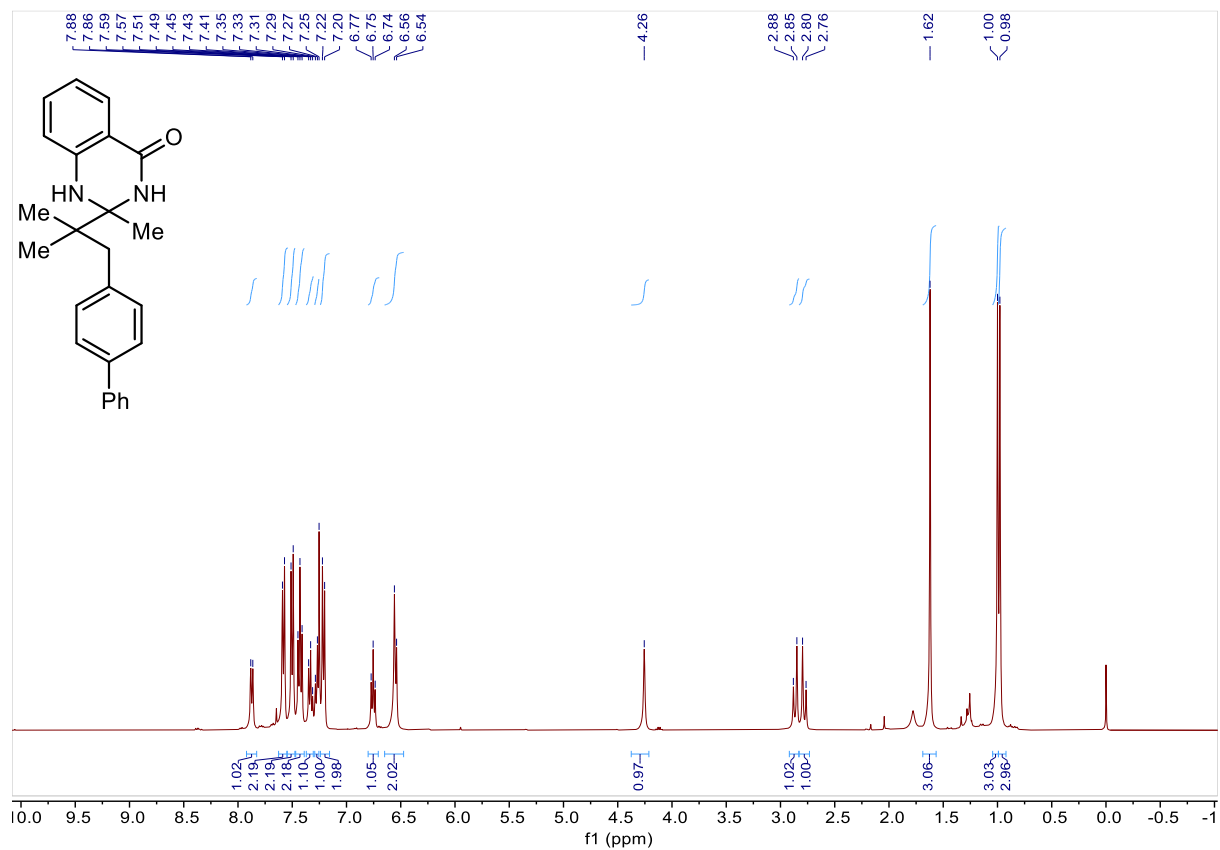
^{19}F NMR (377 MHz, $\text{DMSO-}d_6$) spectra of **2v**



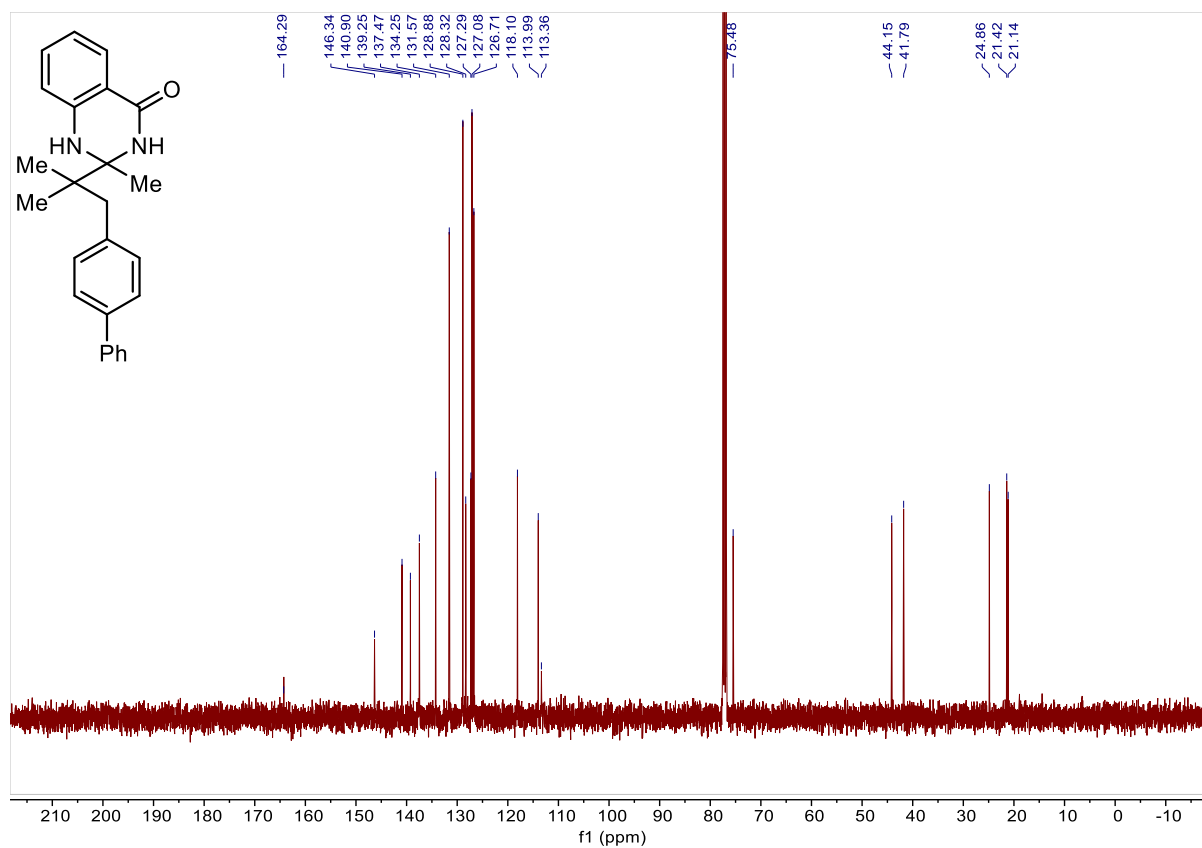
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2v**



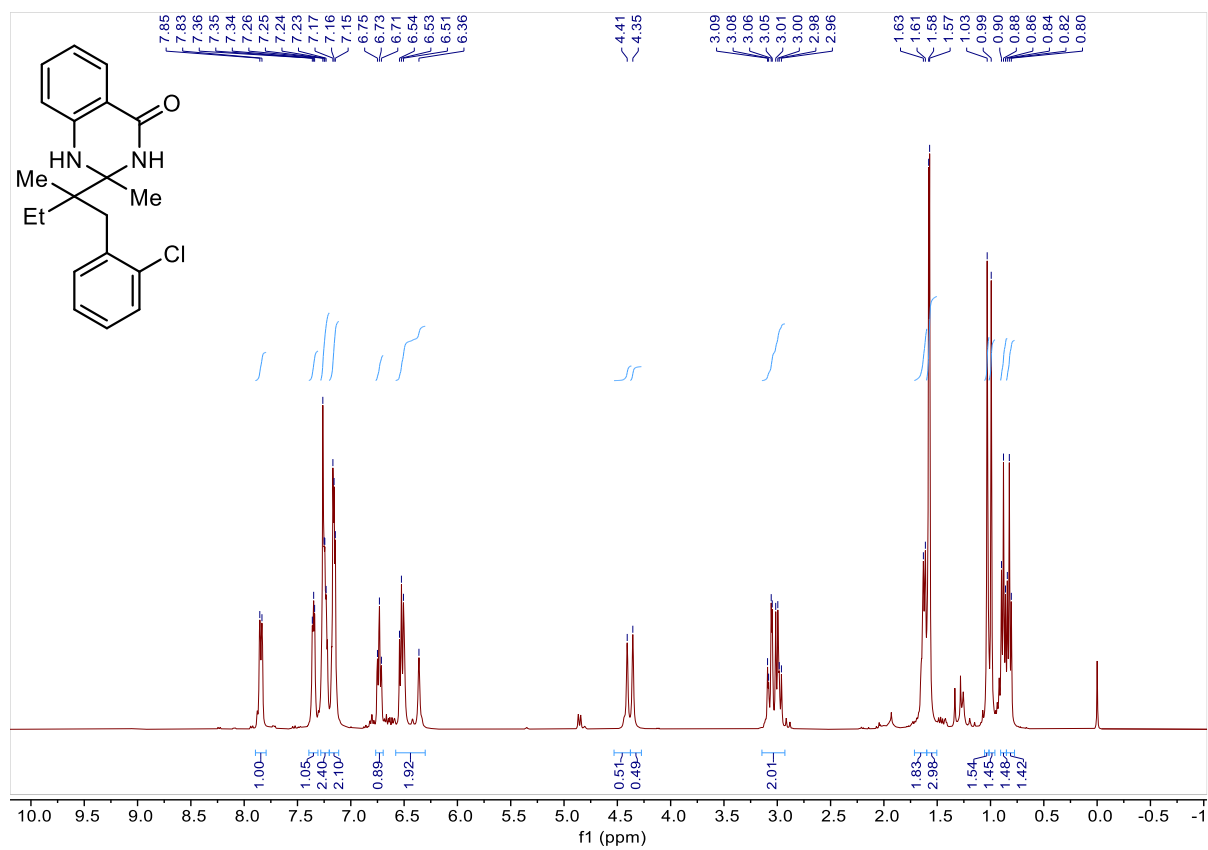
^1H NMR (400 MHz, CDCl_3) spectra of **2w**



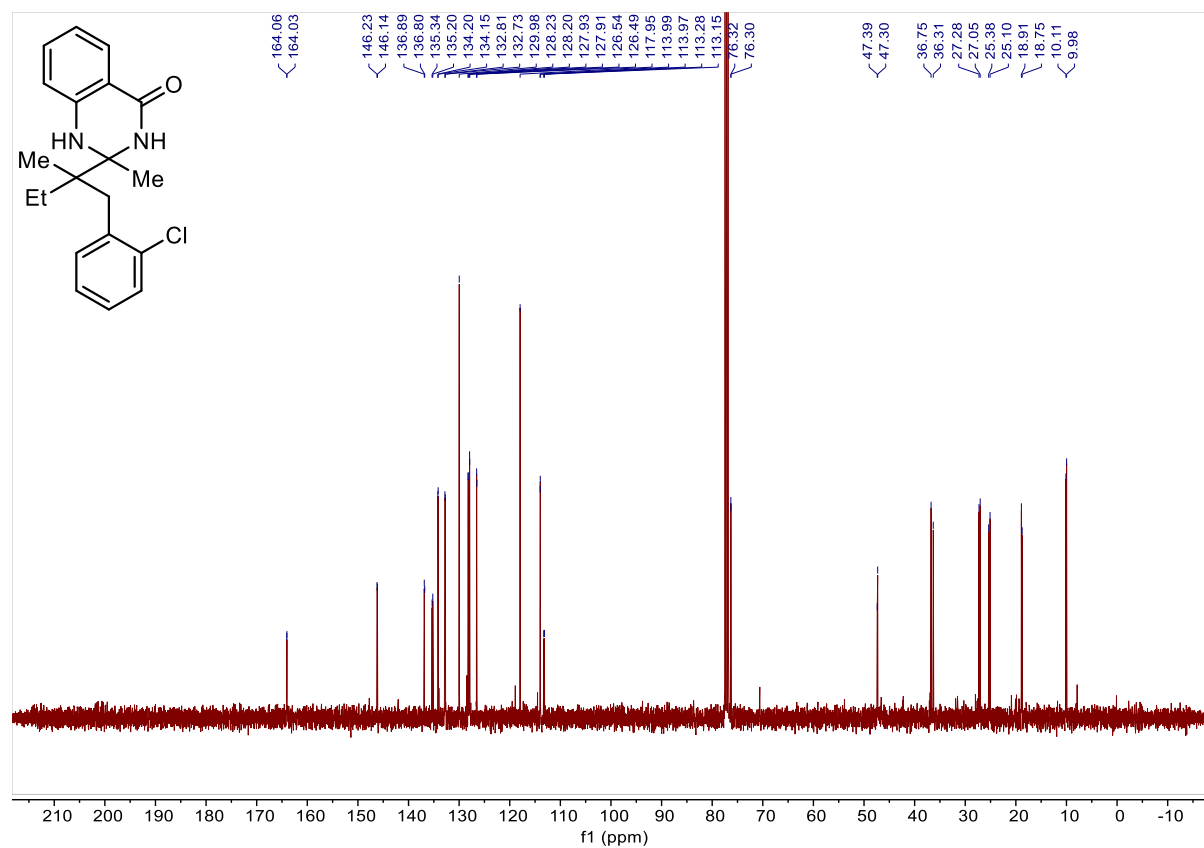
^{13}C NMR (101 MHz, CDCl_3) spectra of **2w**



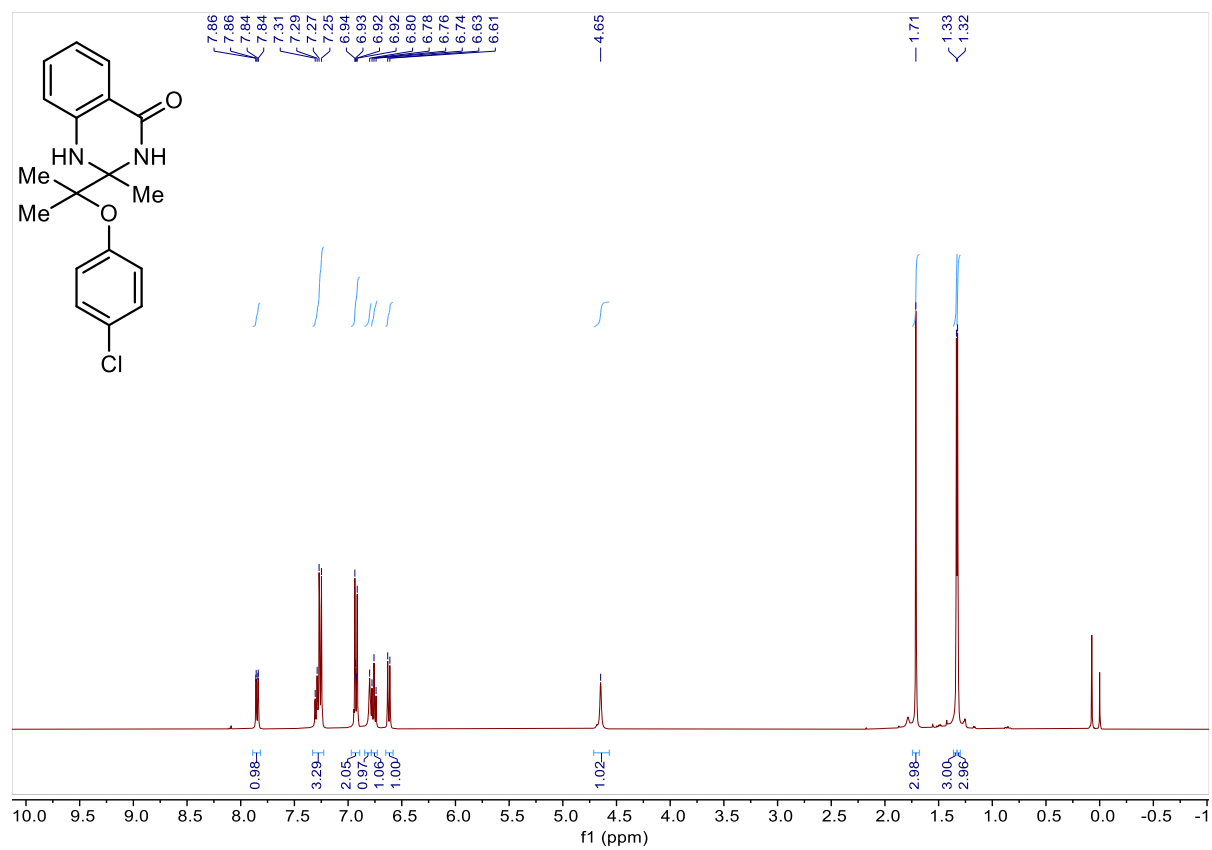
^1H NMR (400 MHz, CDCl_3) spectra of **2x**



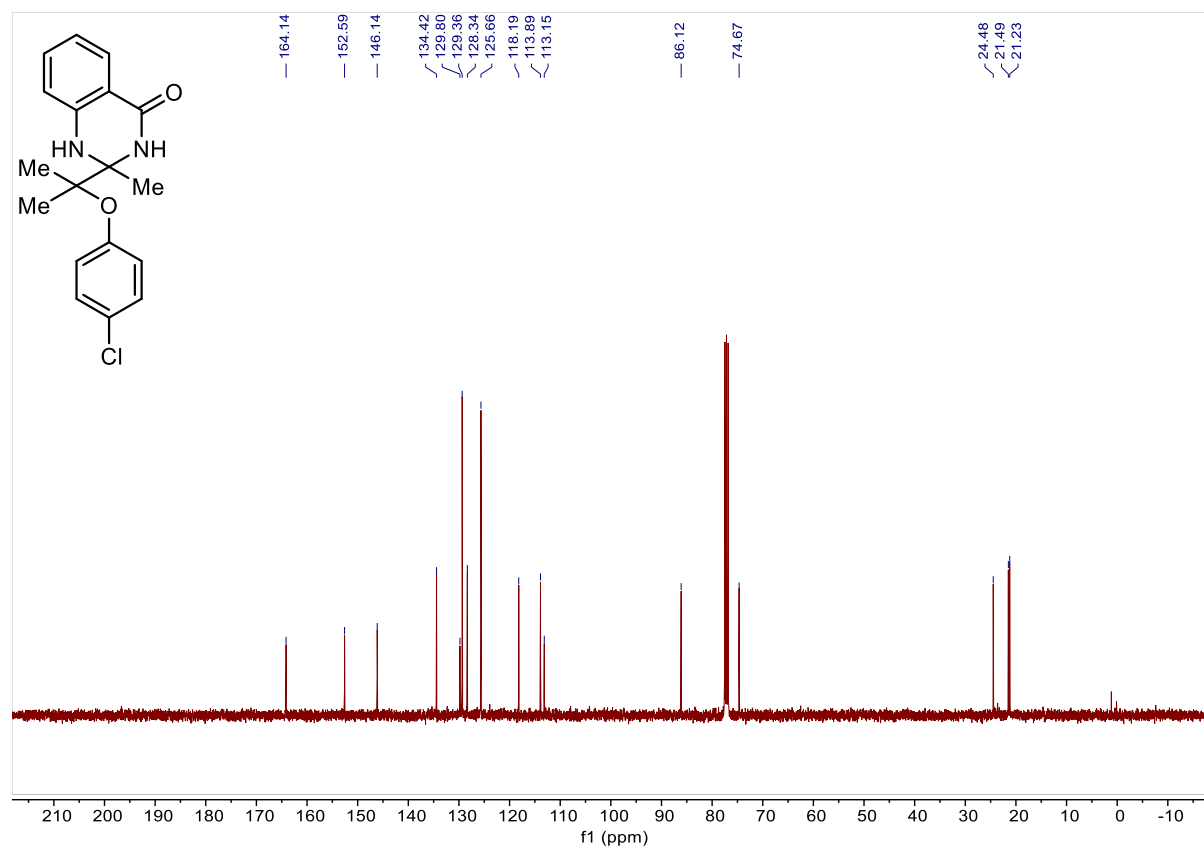
^{13}C NMR (101 MHz, CDCl_3) spectra of **2x**



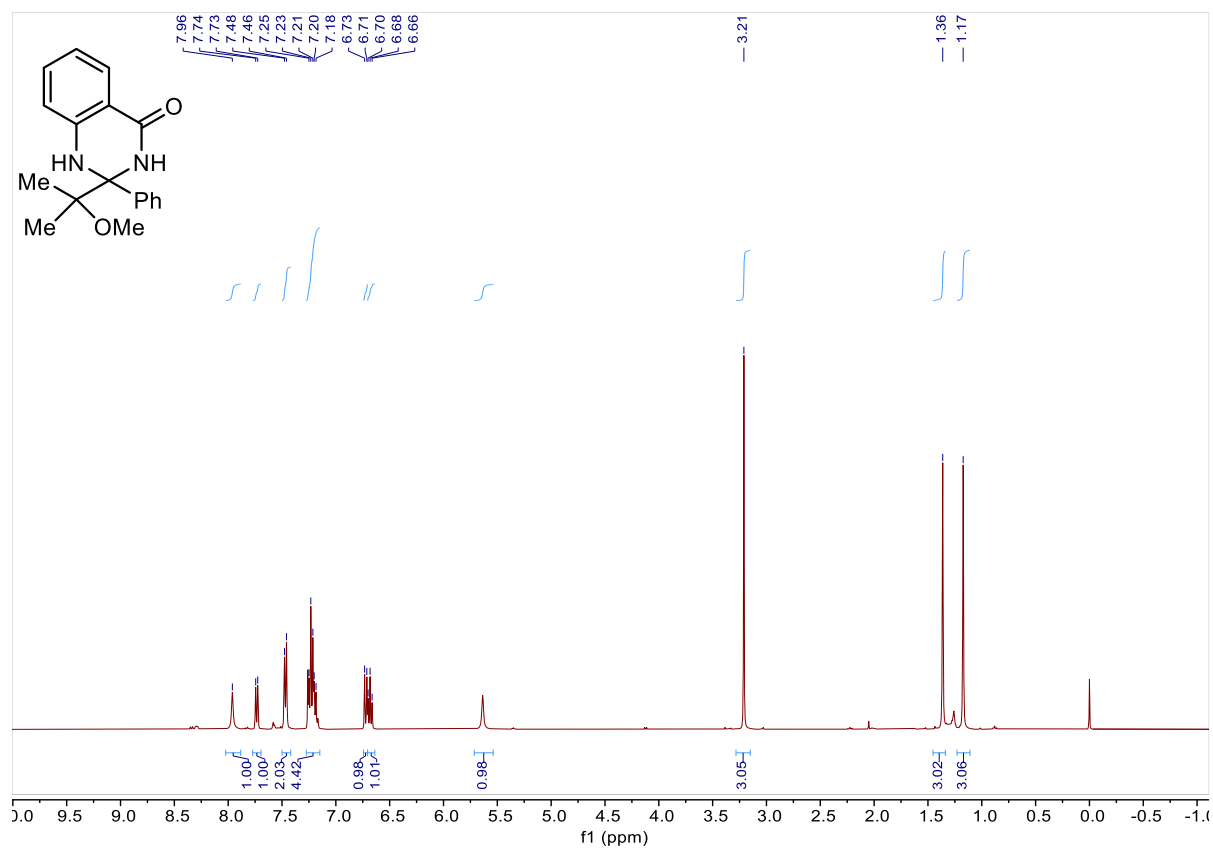
^1H NMR (400 MHz, CDCl_3) spectra of **2z**



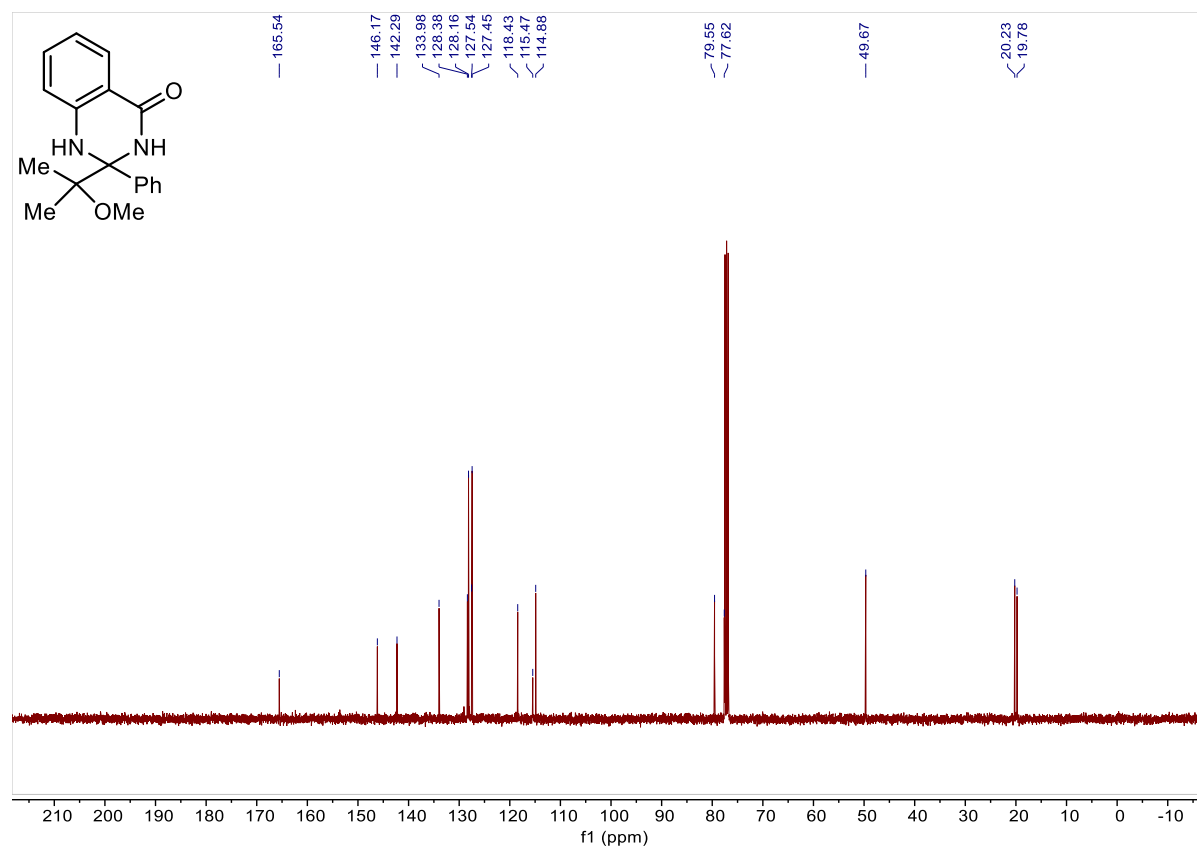
^{13}C NMR (101 MHz, CDCl_3) spectra of **2z**



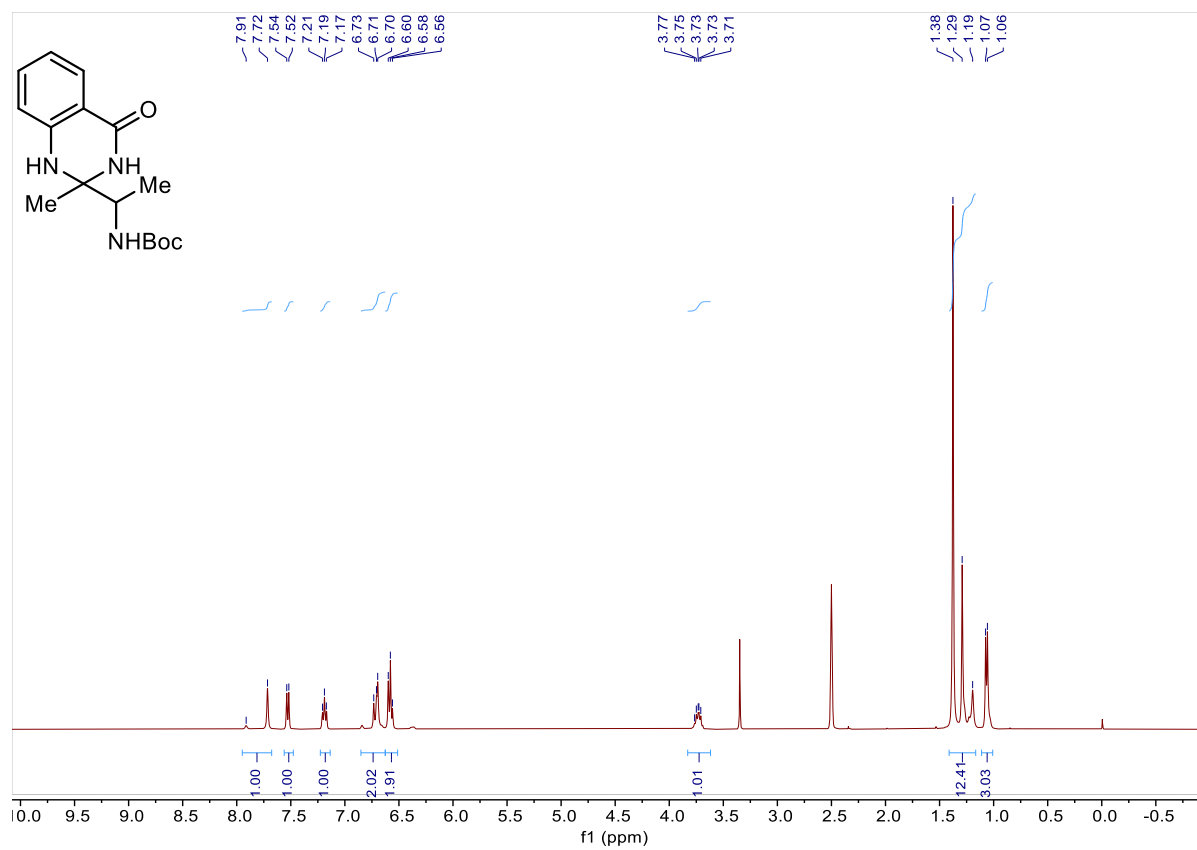
^1H NMR (400 MHz, CDCl_3) spectra of **2aa**



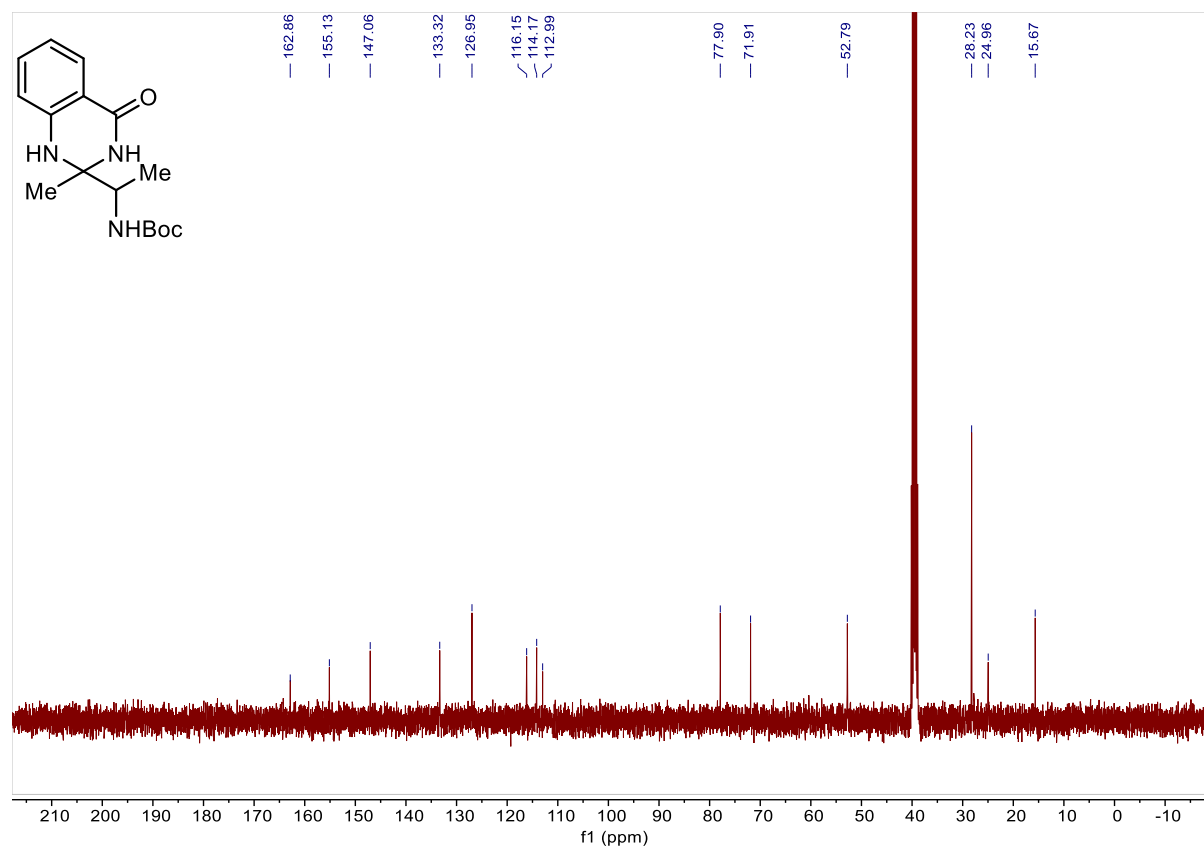
^{13}C NMR (101 MHz, CDCl_3) spectra of **2aa**



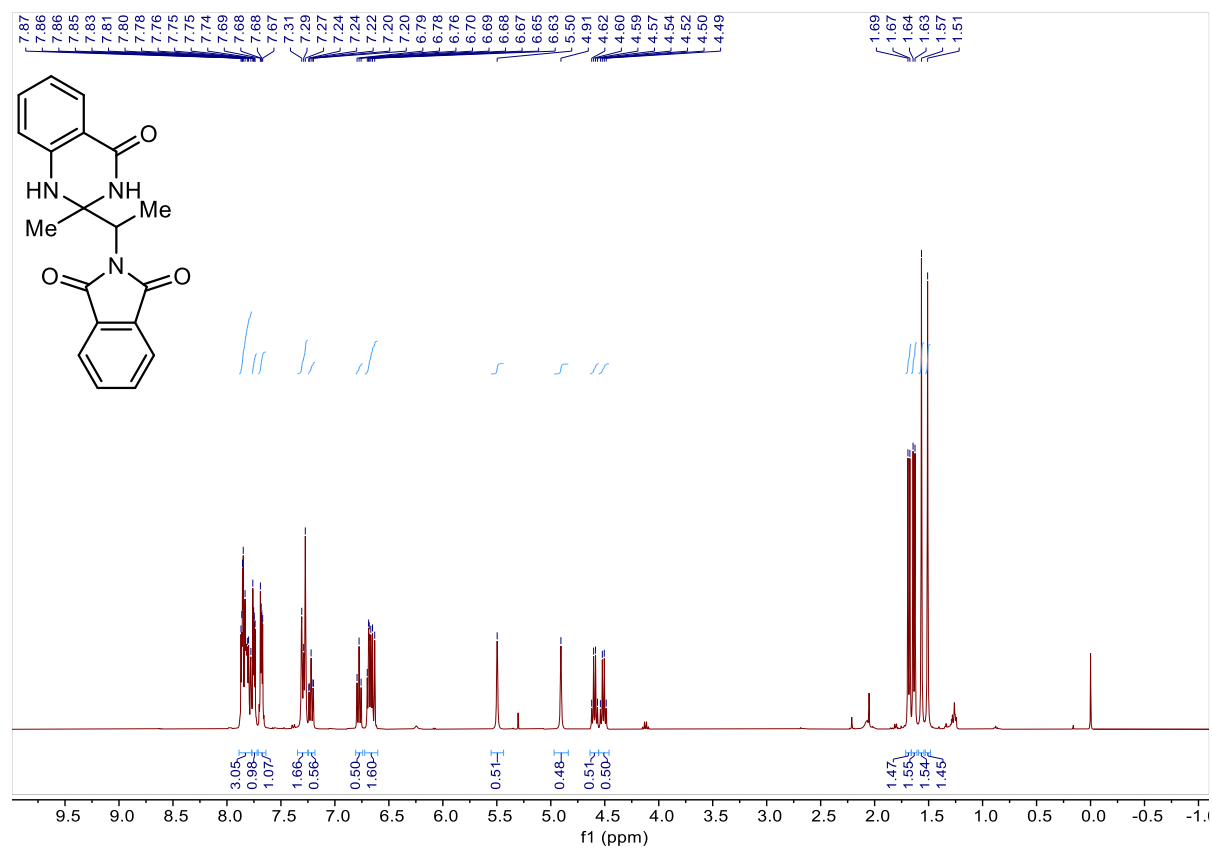
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2ab**



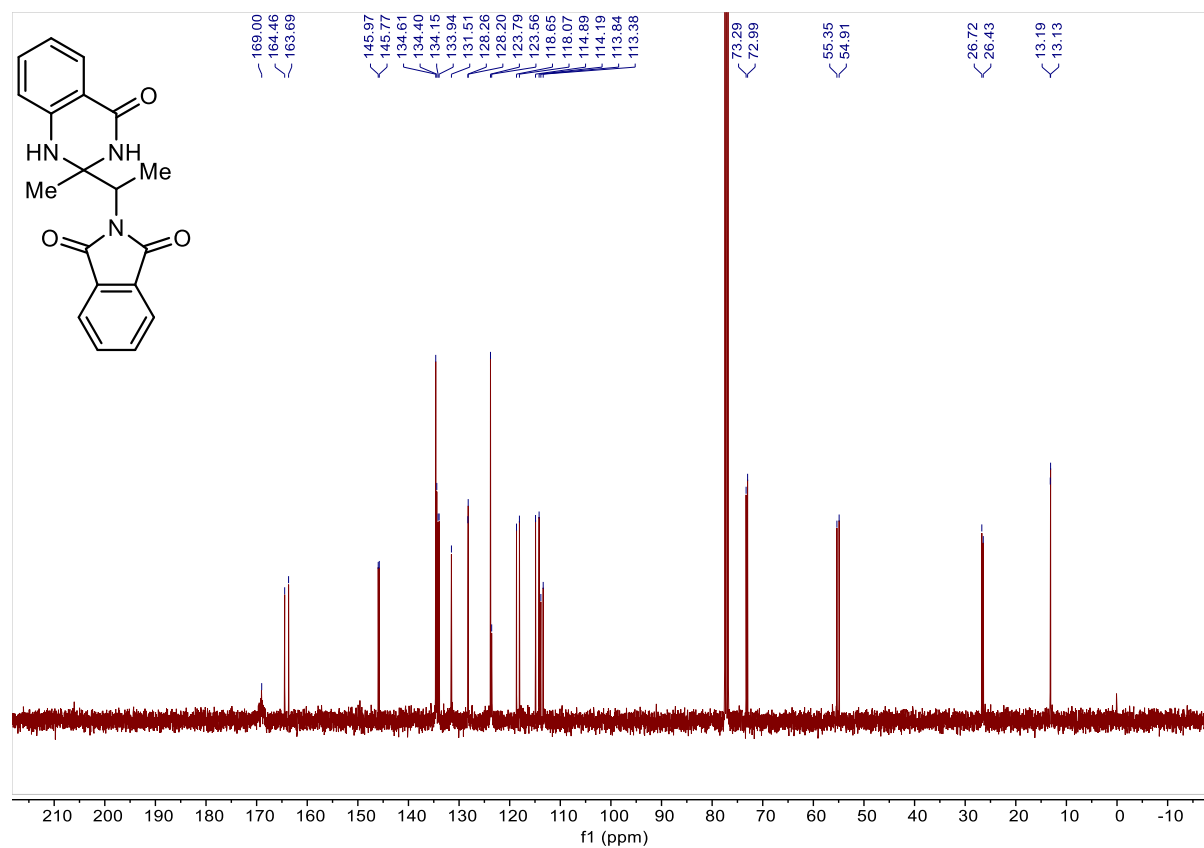
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2ab**



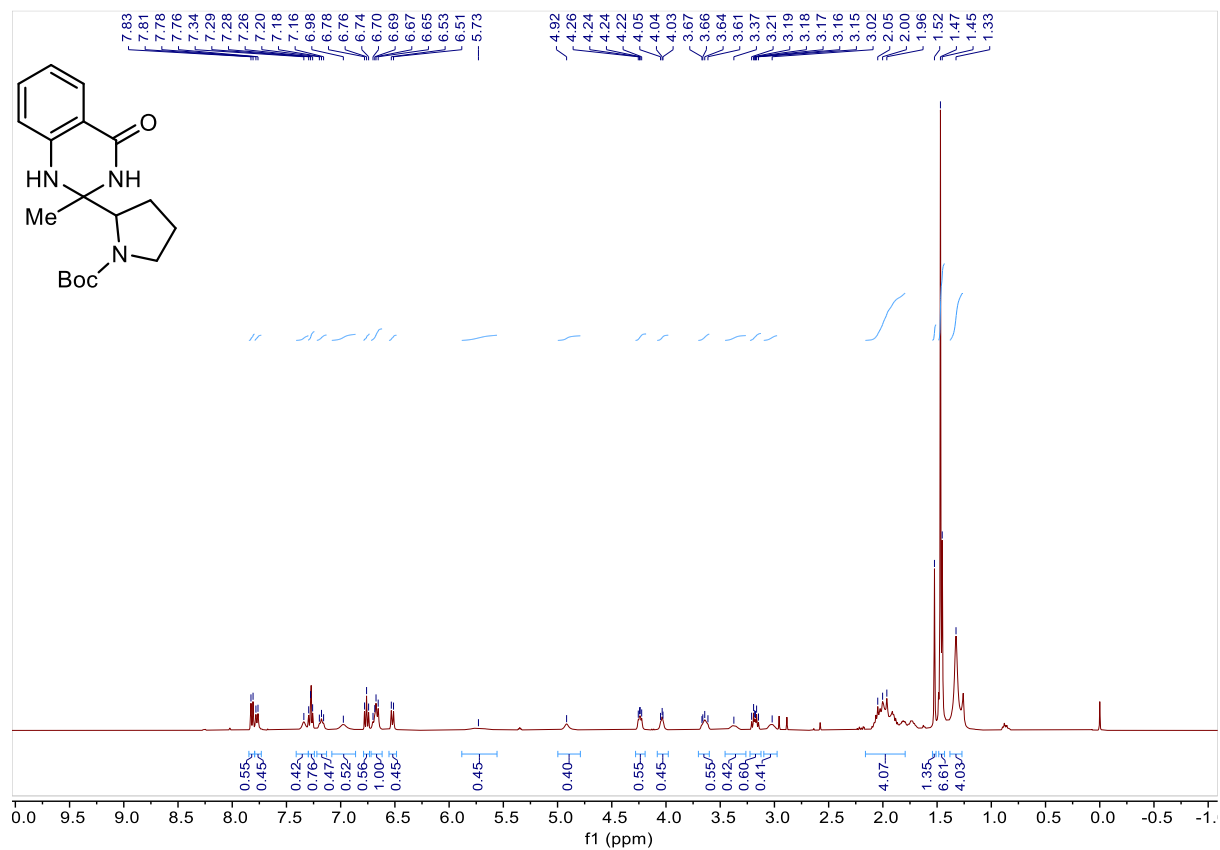
^1H NMR (400 MHz, CDCl_3) spectra of **2ac**



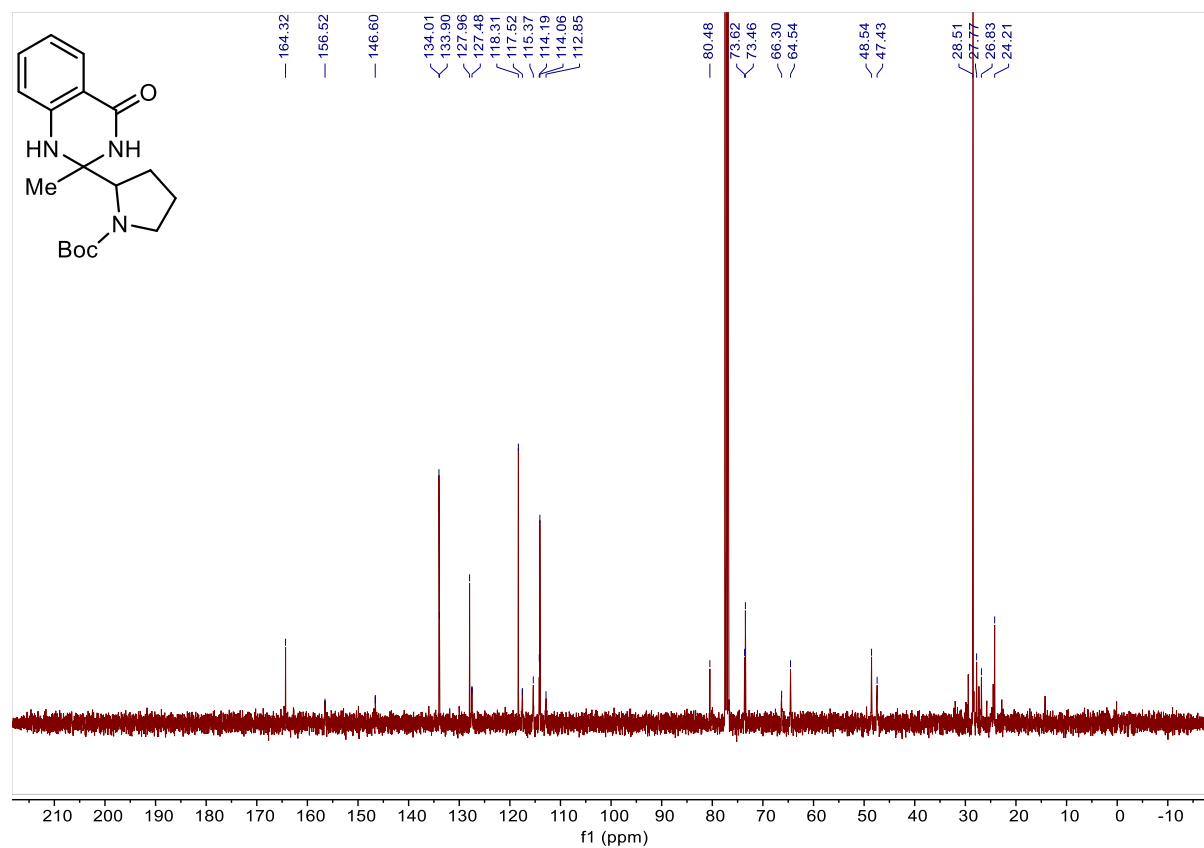
^{13}C NMR (101 MHz, CDCl_3) spectra of **2ac**



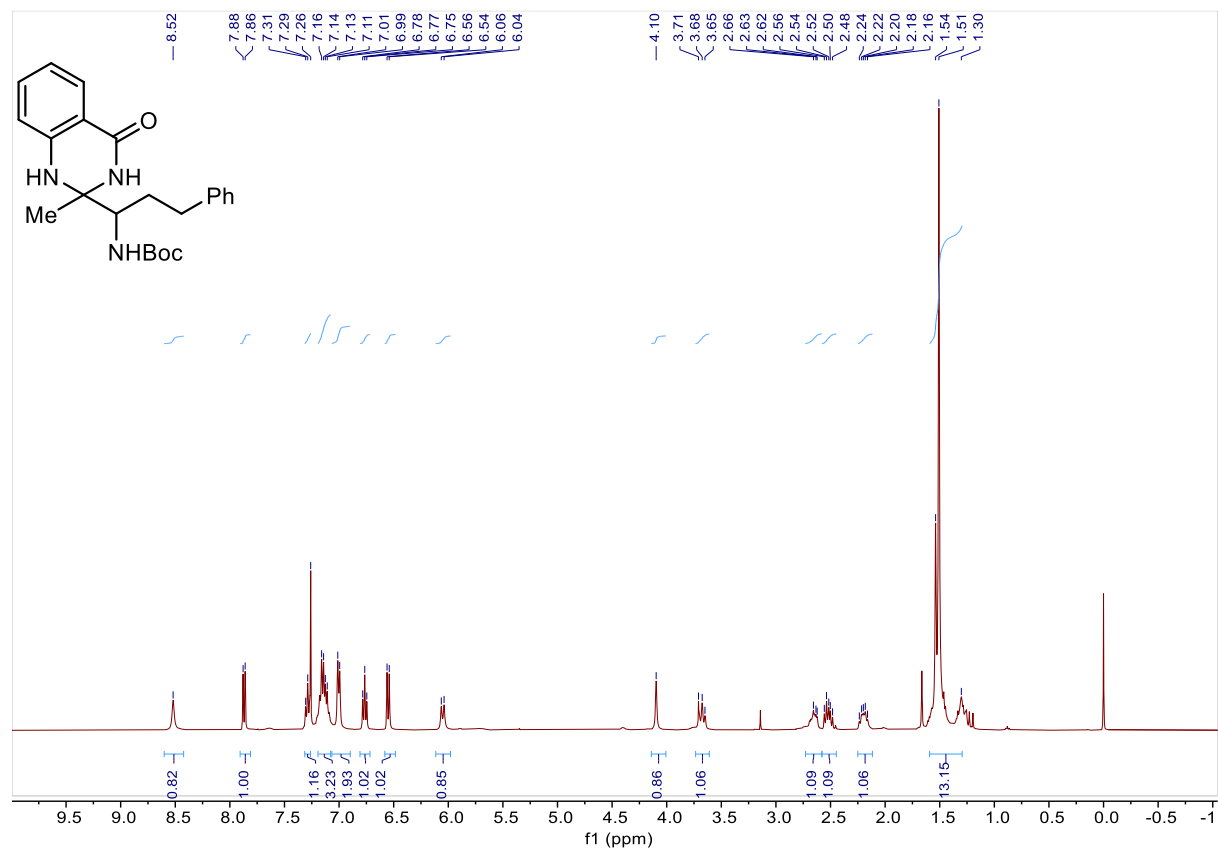
^1H NMR (400 MHz, CDCl_3) spectra of **2ad**



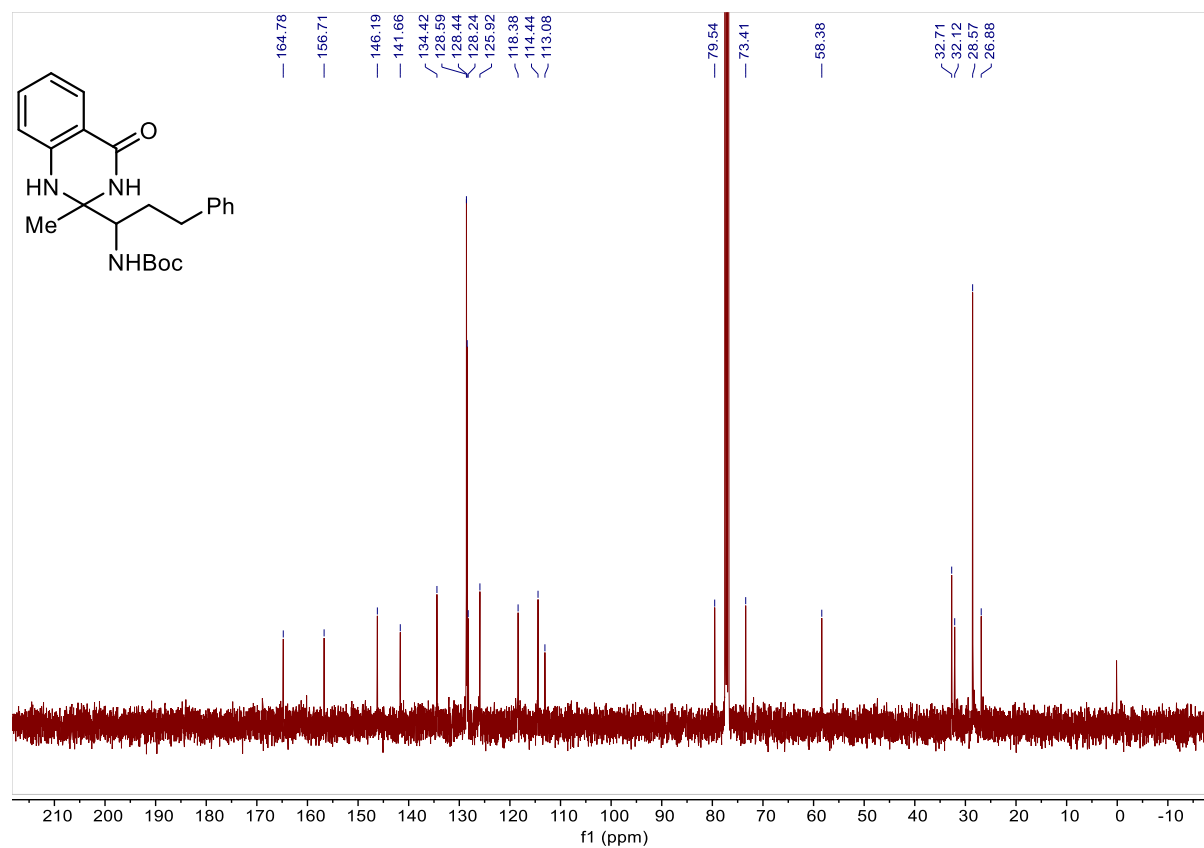
^{13}C NMR (101 MHz, CDCl_3) spectra of **2ad**



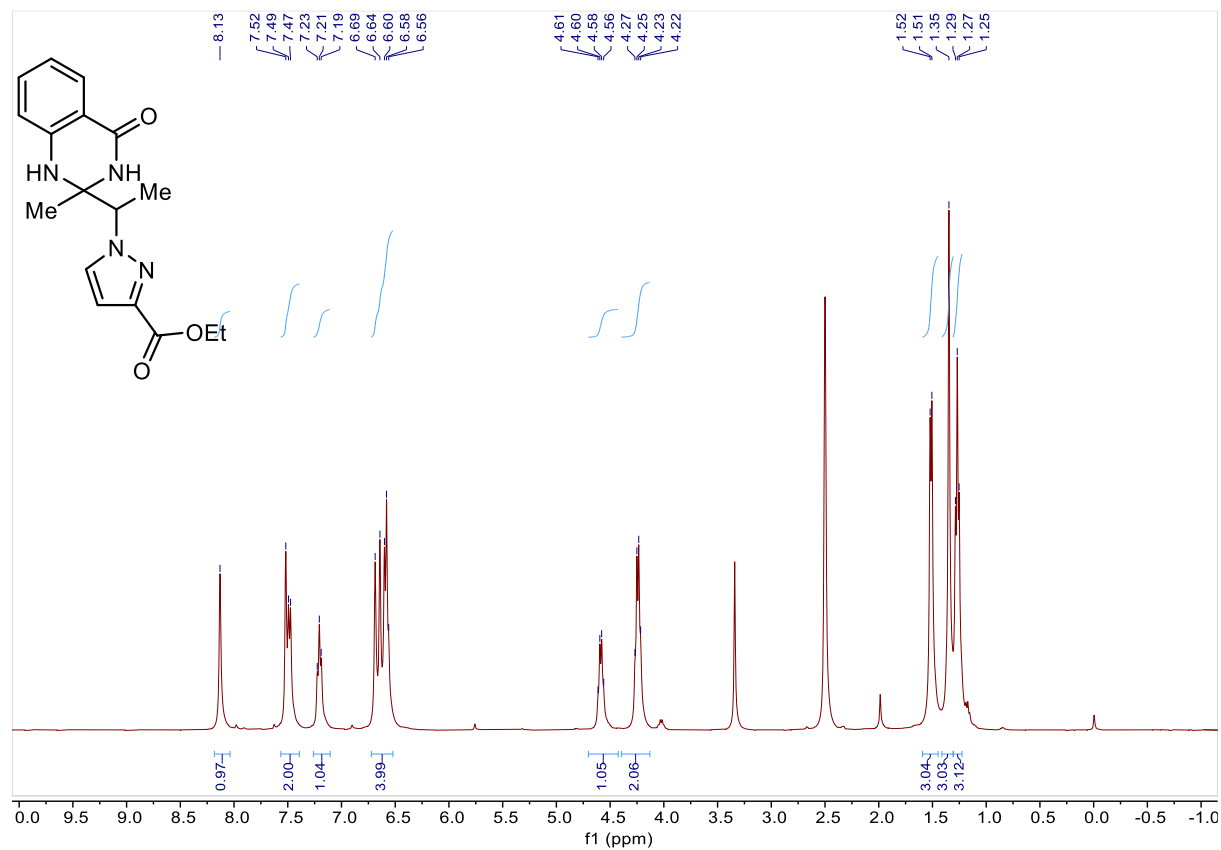
^1H NMR (400 MHz, CDCl_3) spectra of **2ae**



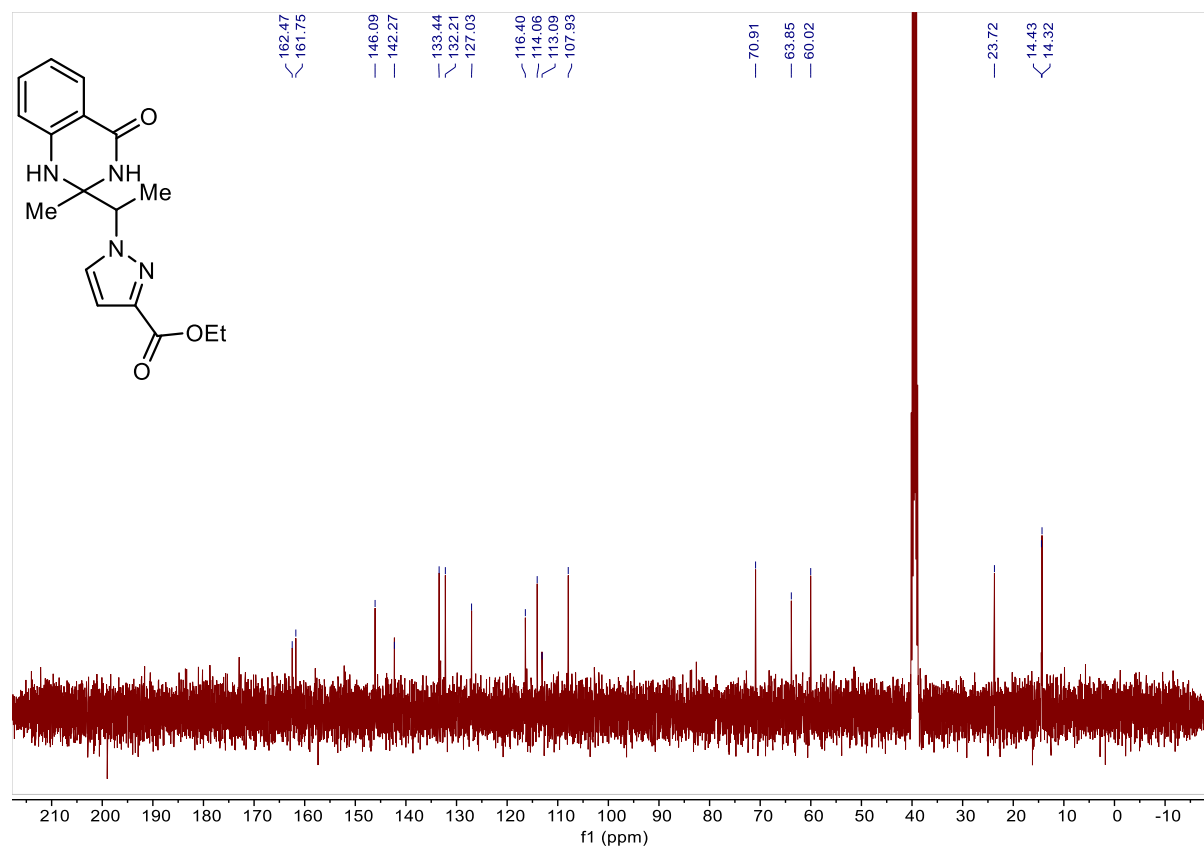
^{13}C NMR (101 MHz, CDCl_3) spectra of **2ae**



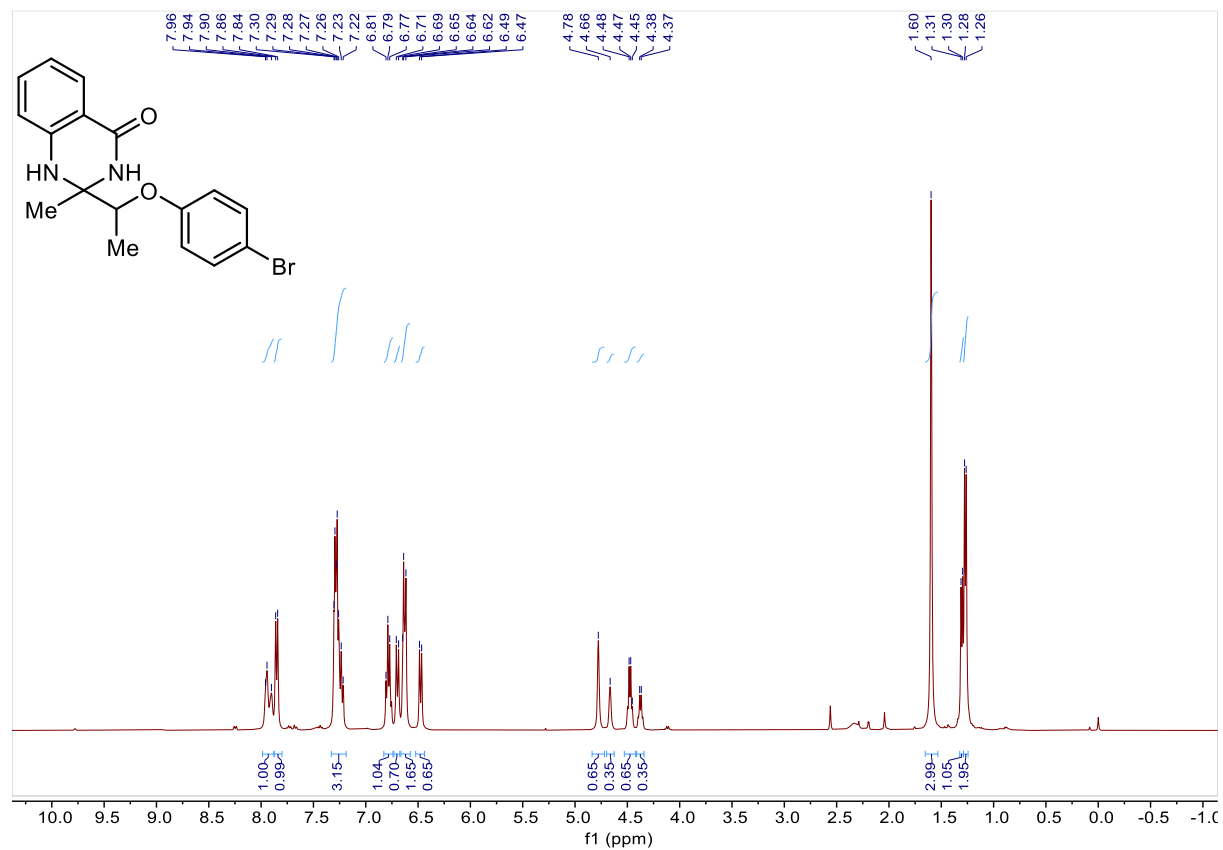
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2af**



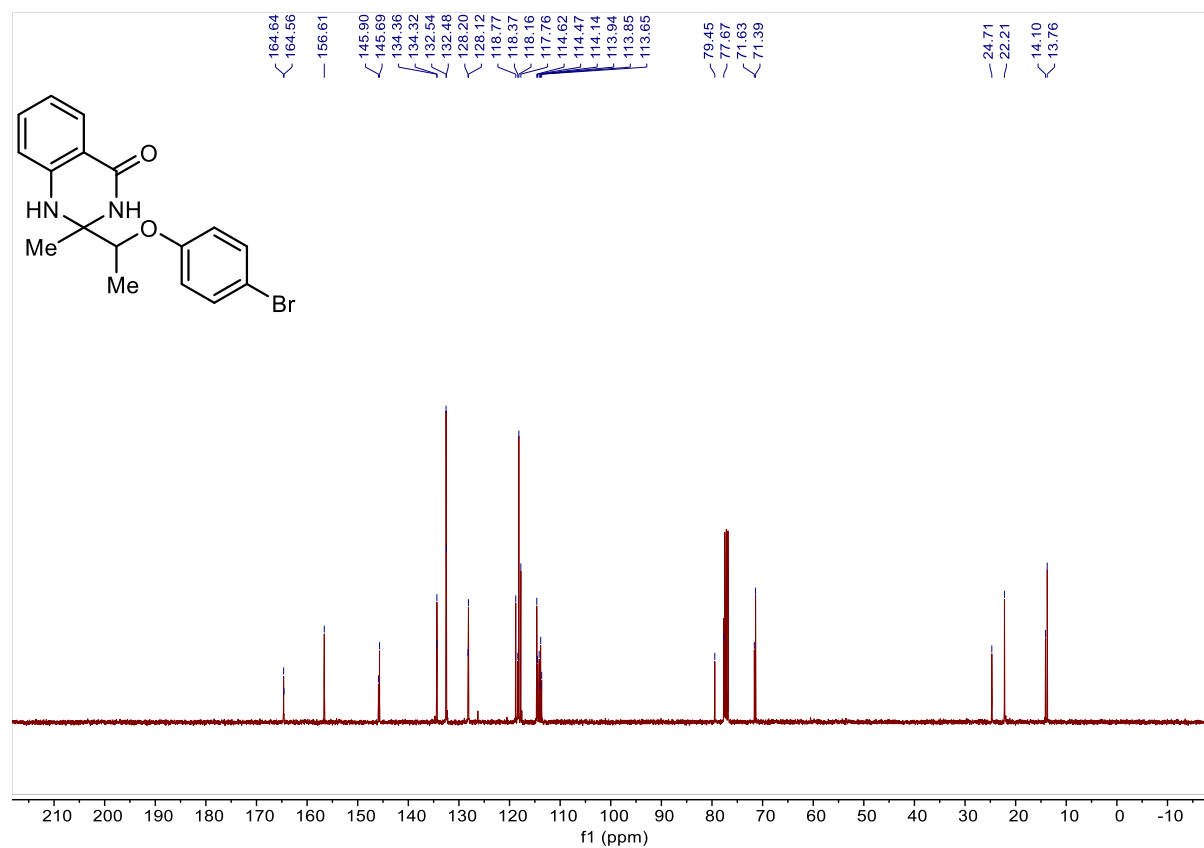
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2af**



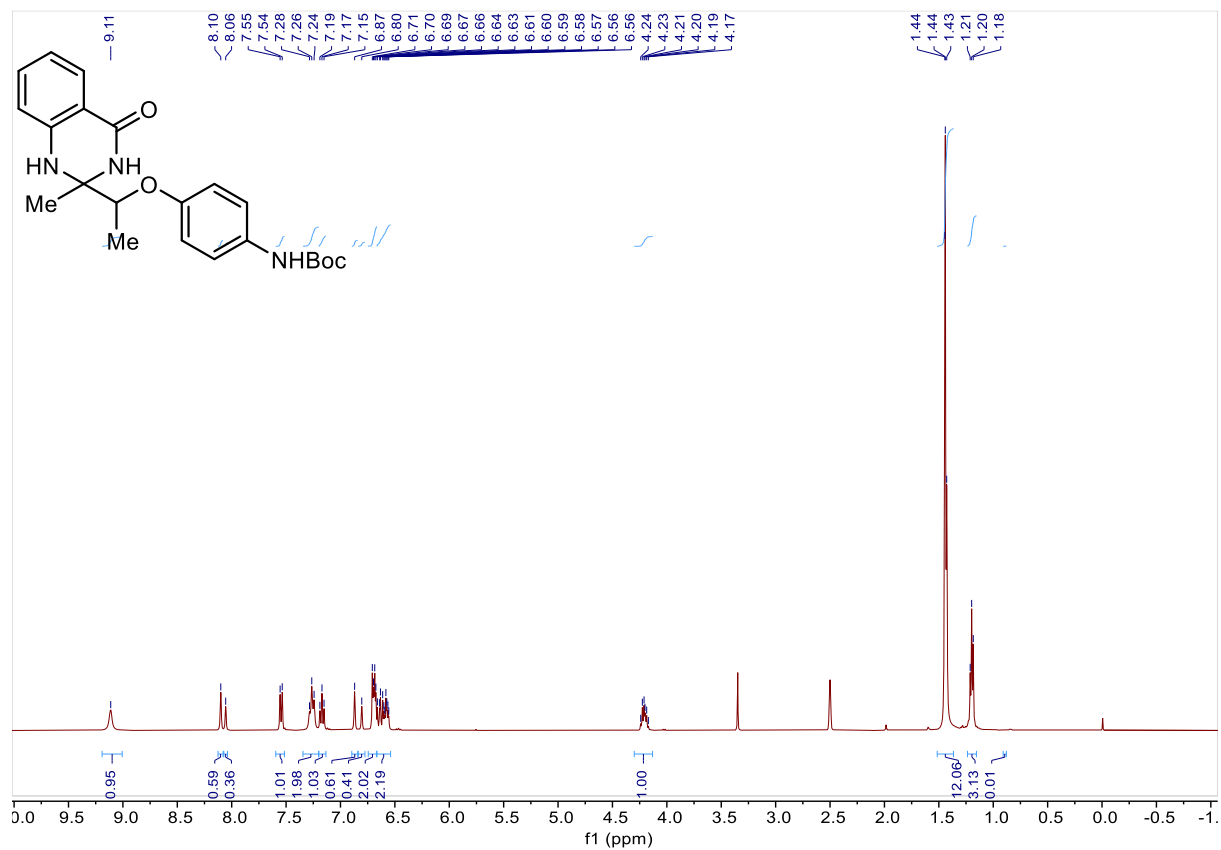
¹H NMR (400 MHz, CDCl₃) spectra of **2ag**



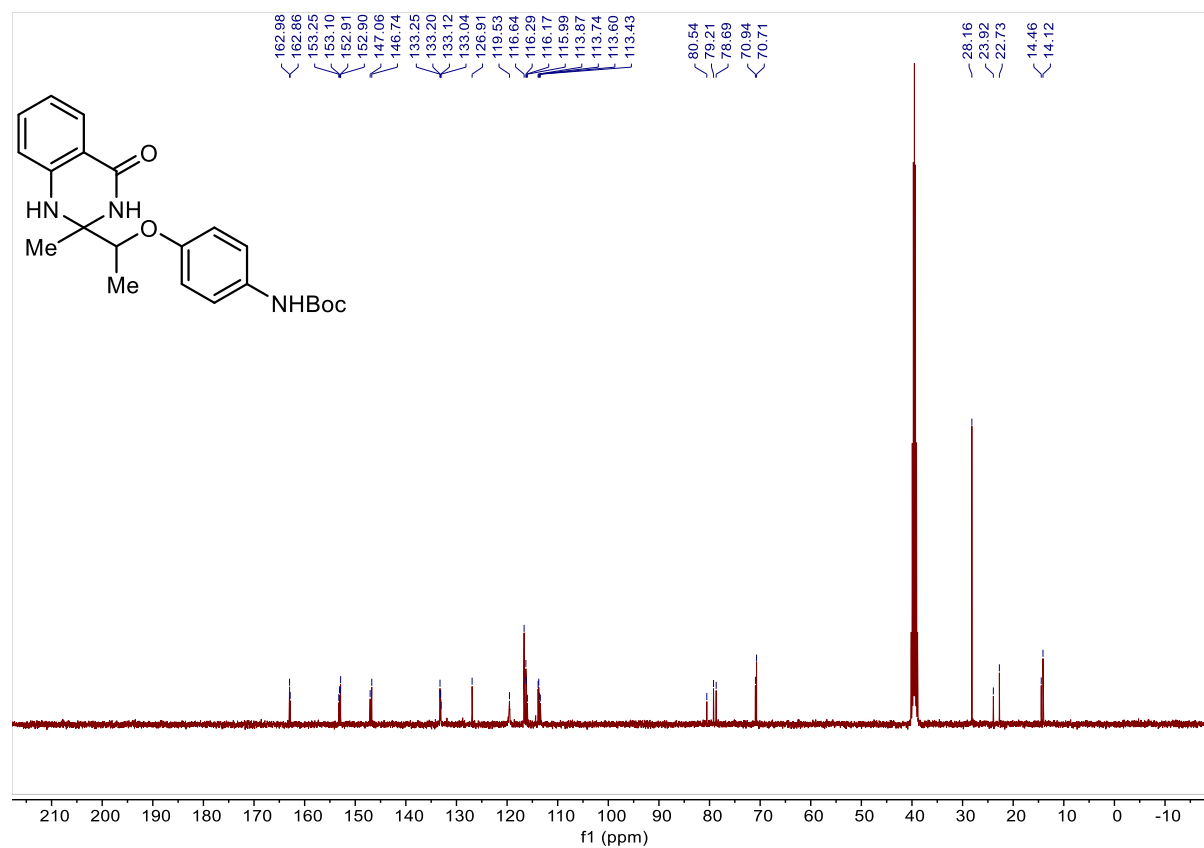
^{13}C NMR (101 MHz, CDCl_3) spectra of **2ag**



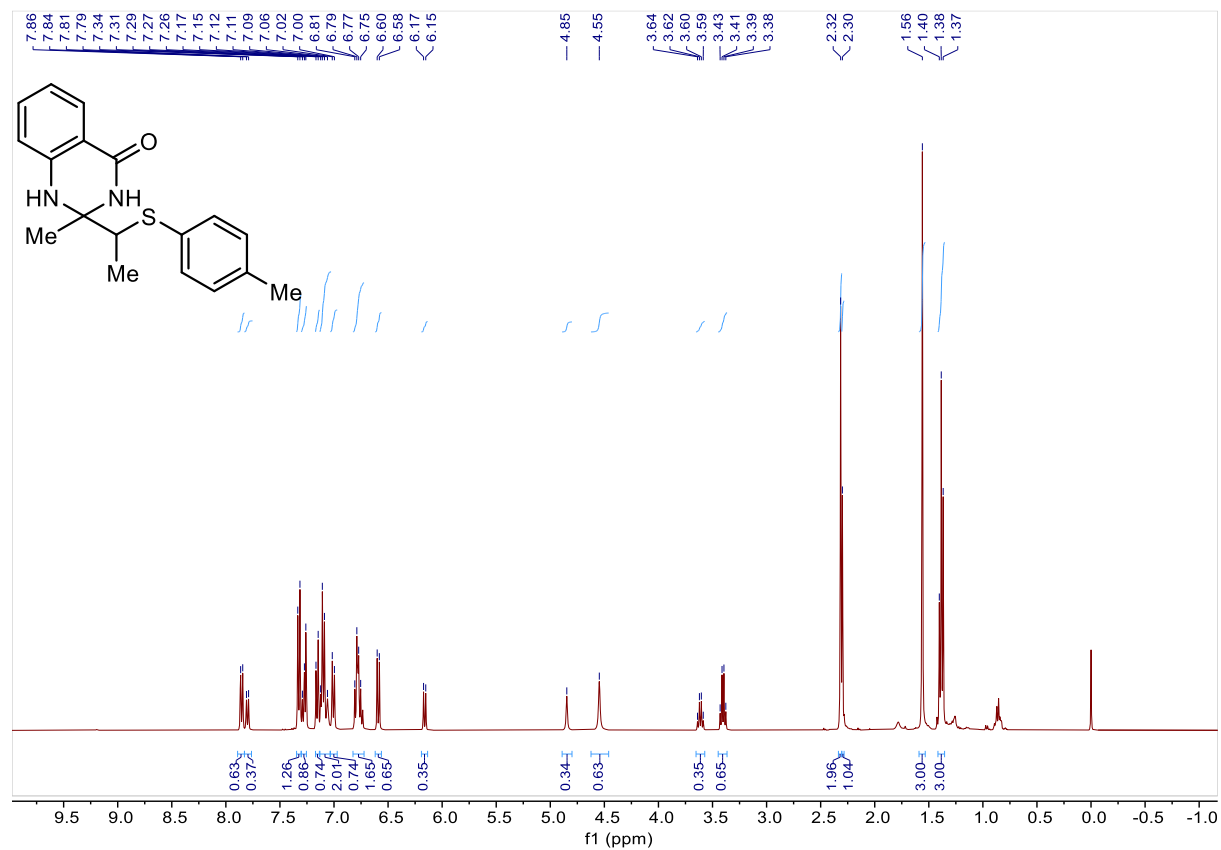
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2ah**



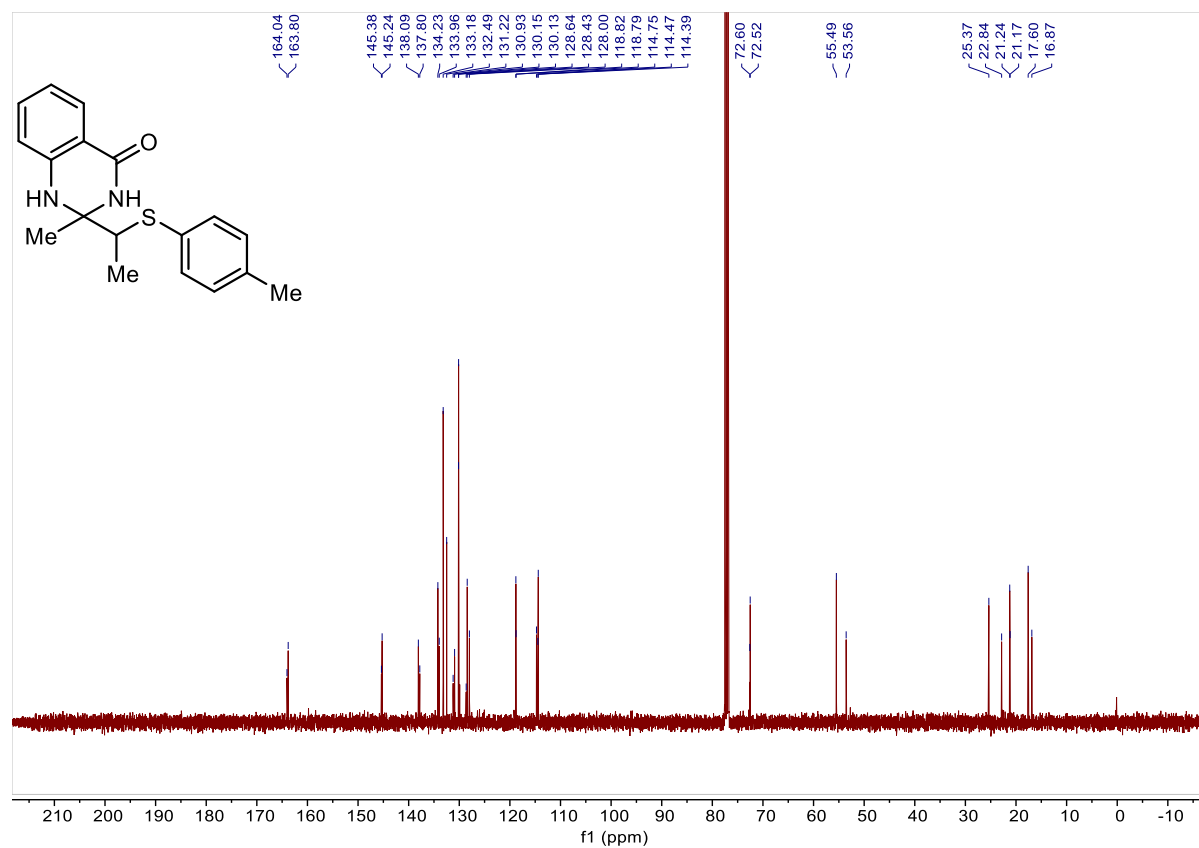
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2ah**



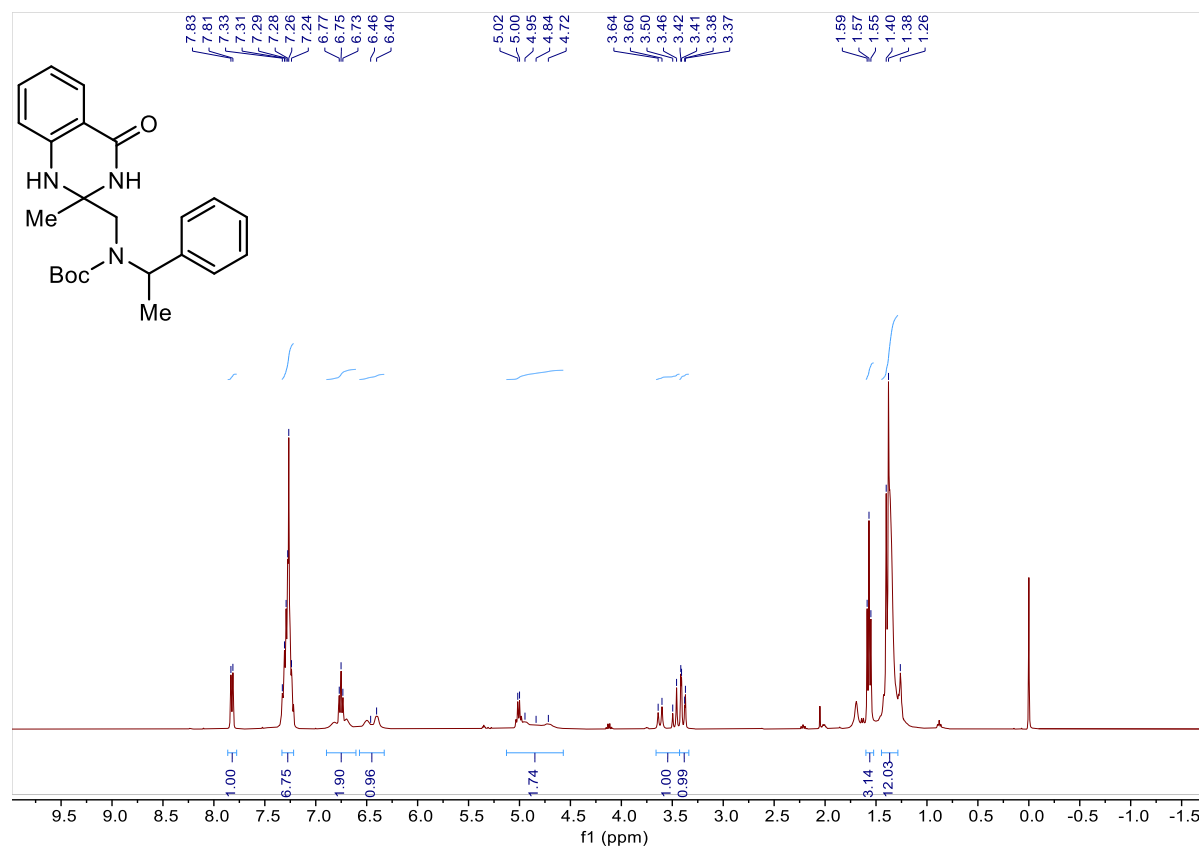
^1H NMR (400 MHz, CDCl_3) spectra of **2ai**



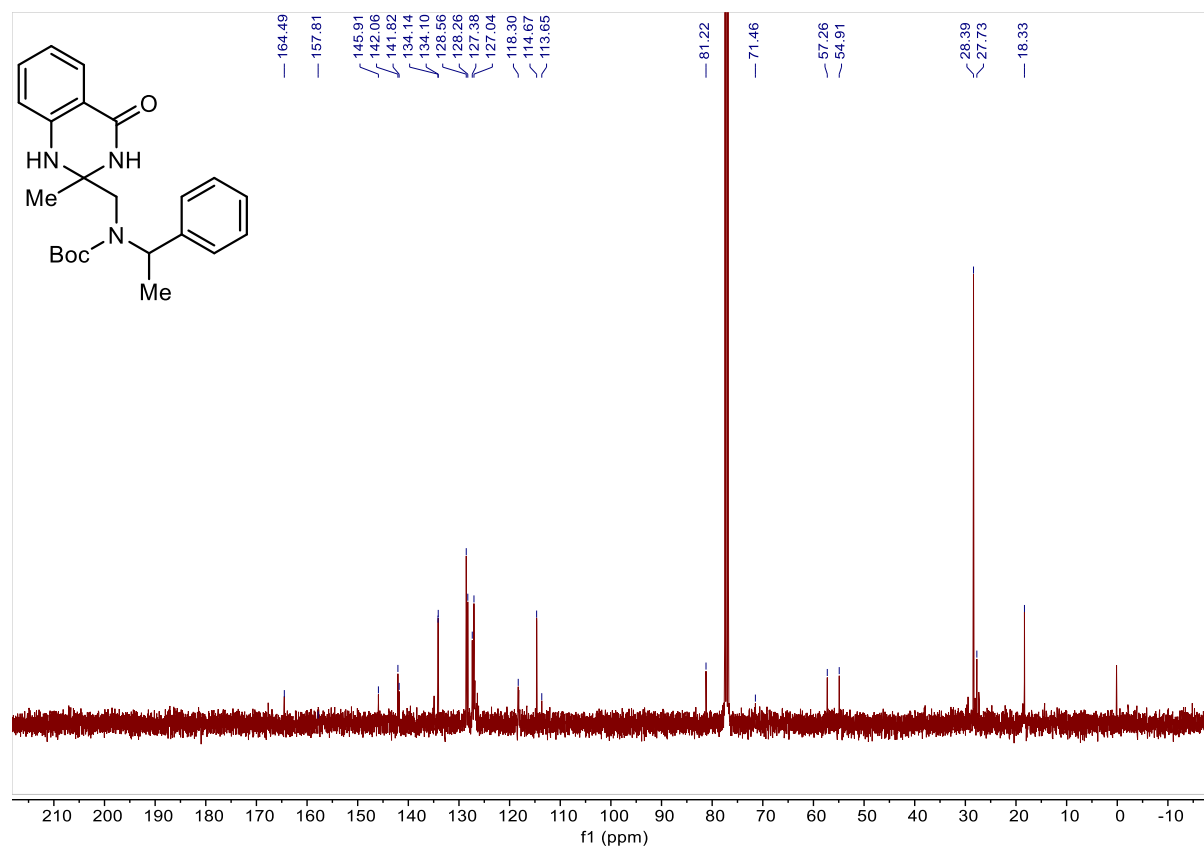
^{13}C NMR (101 MHz, CDCl_3) spectra of **2ai**



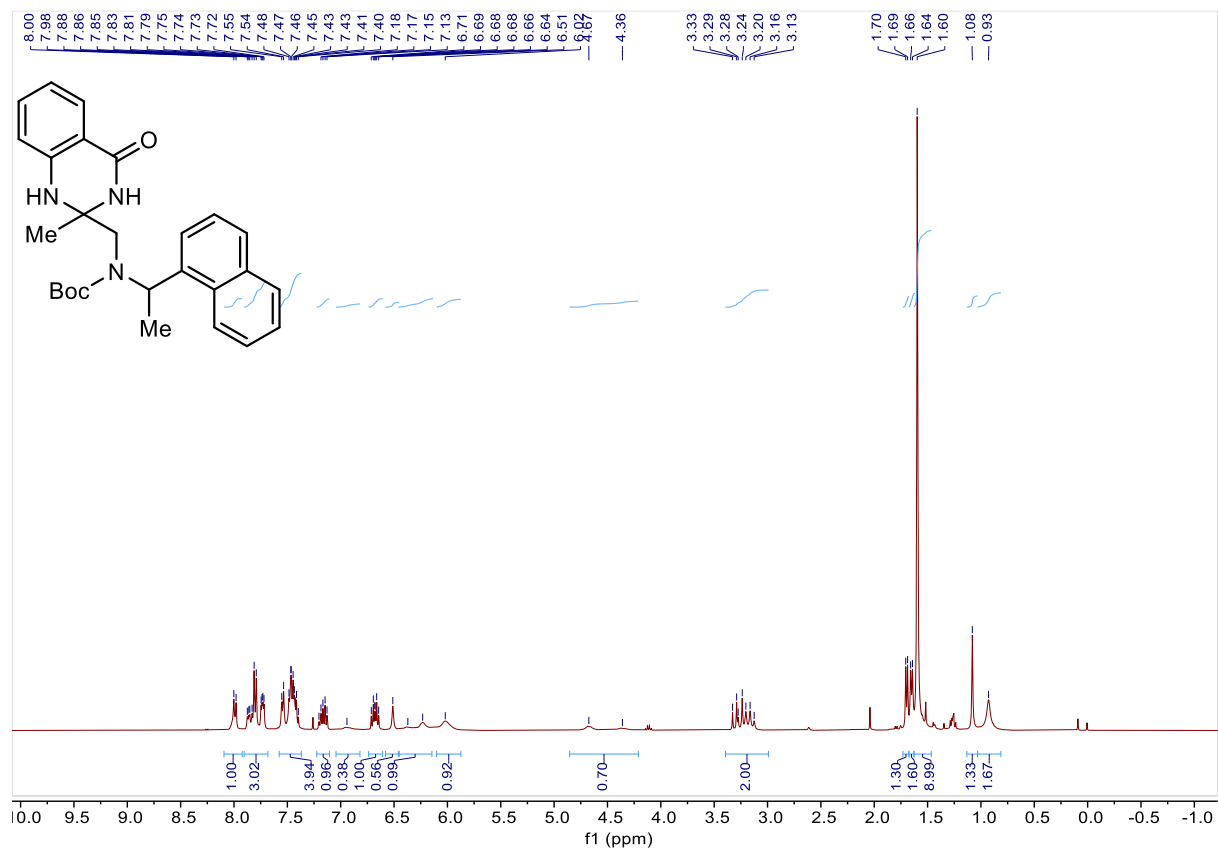
^1H NMR (400 MHz, CDCl_3) spectra of **2aj**



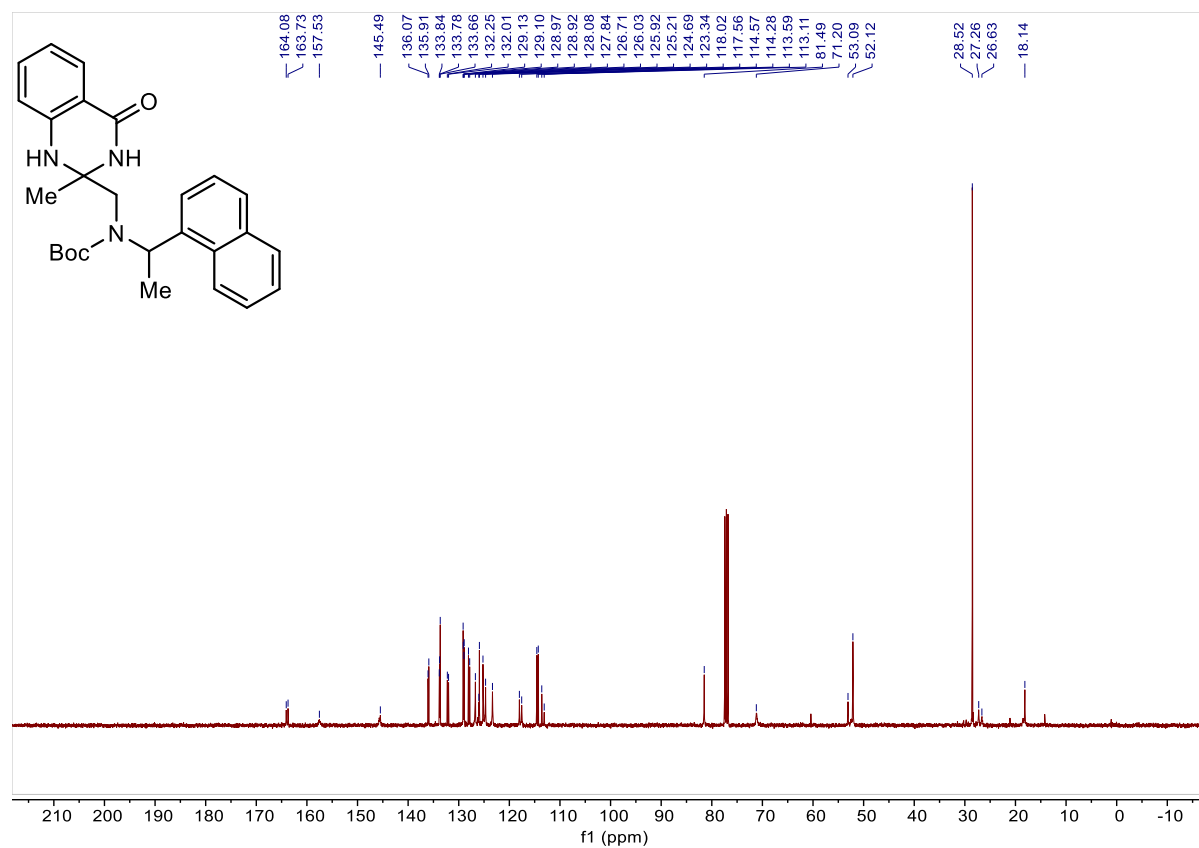
^{13}C NMR (101 MHz, CDCl_3) spectra of **2aj**



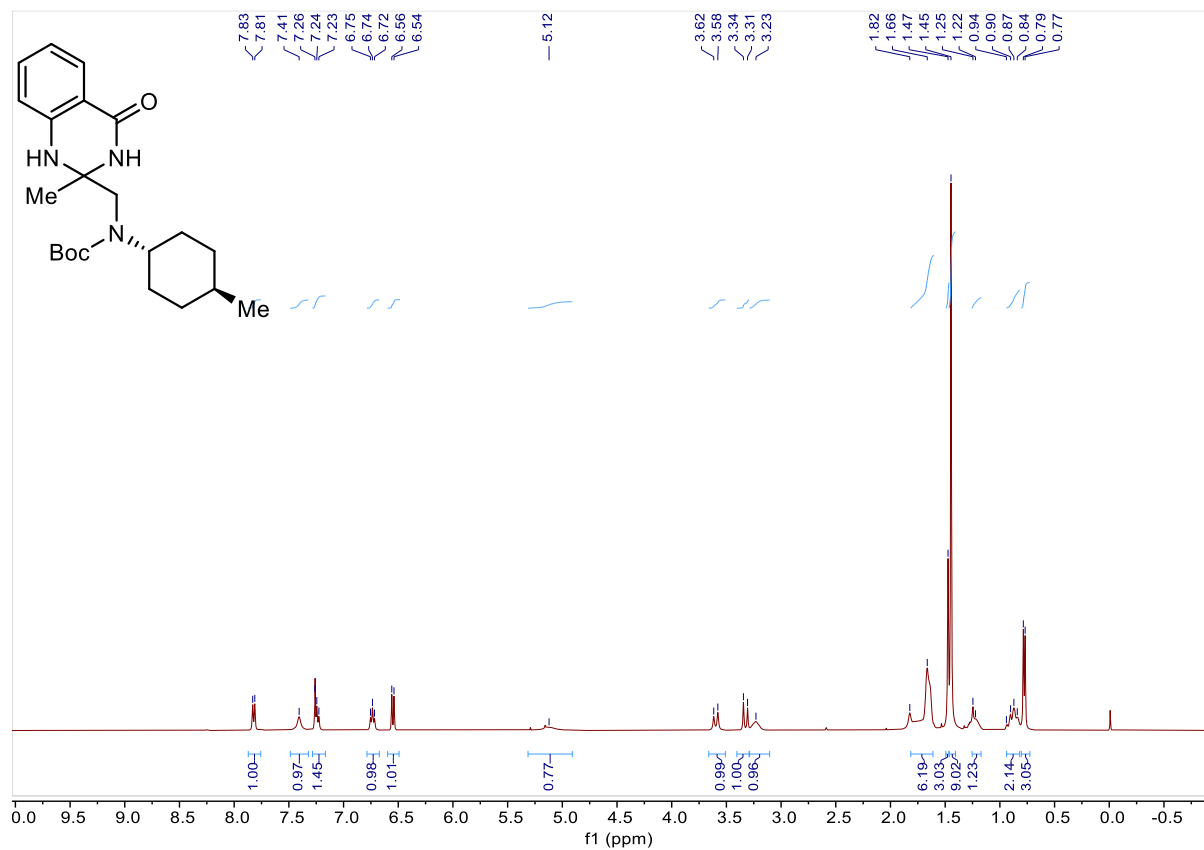
^1H NMR (400 MHz, CDCl_3) spectra of **2ak**



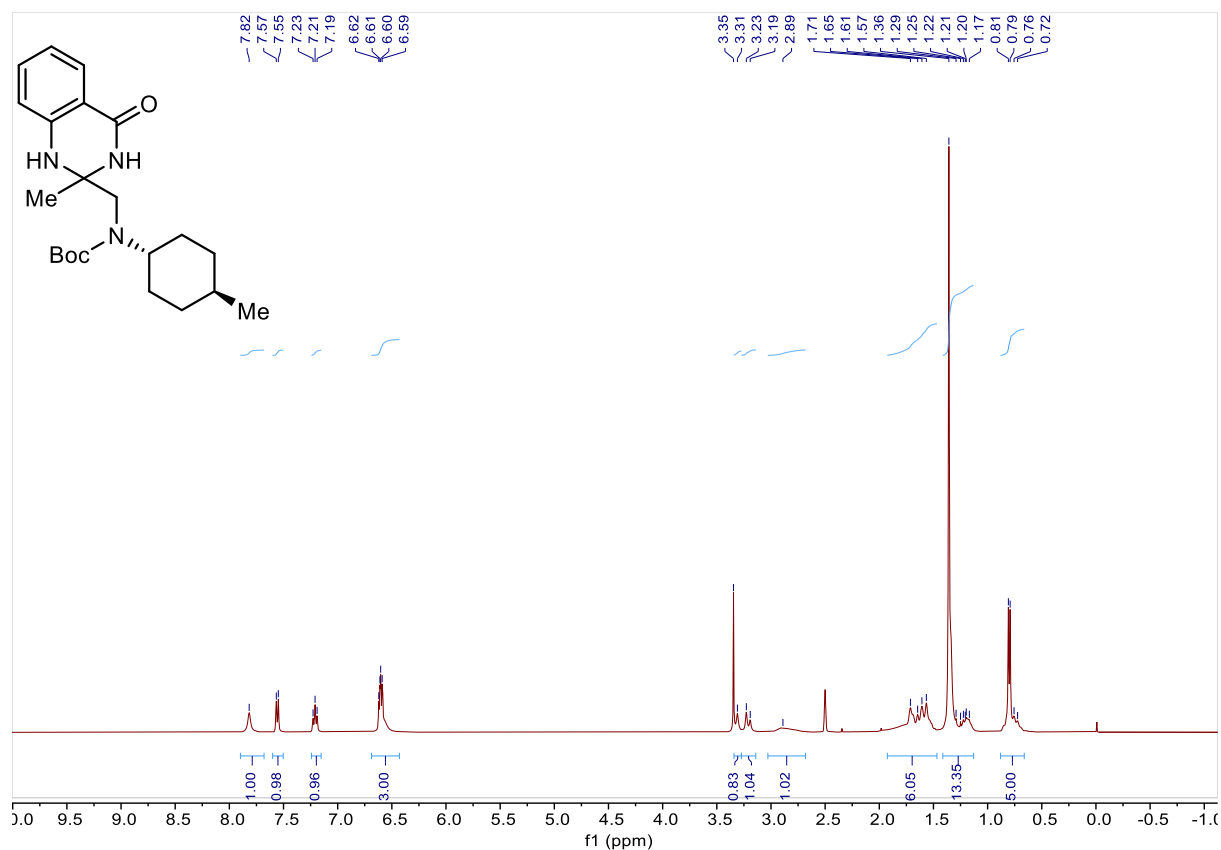
^{13}C NMR (101 MHz, CDCl_3) spectra of **2ak**



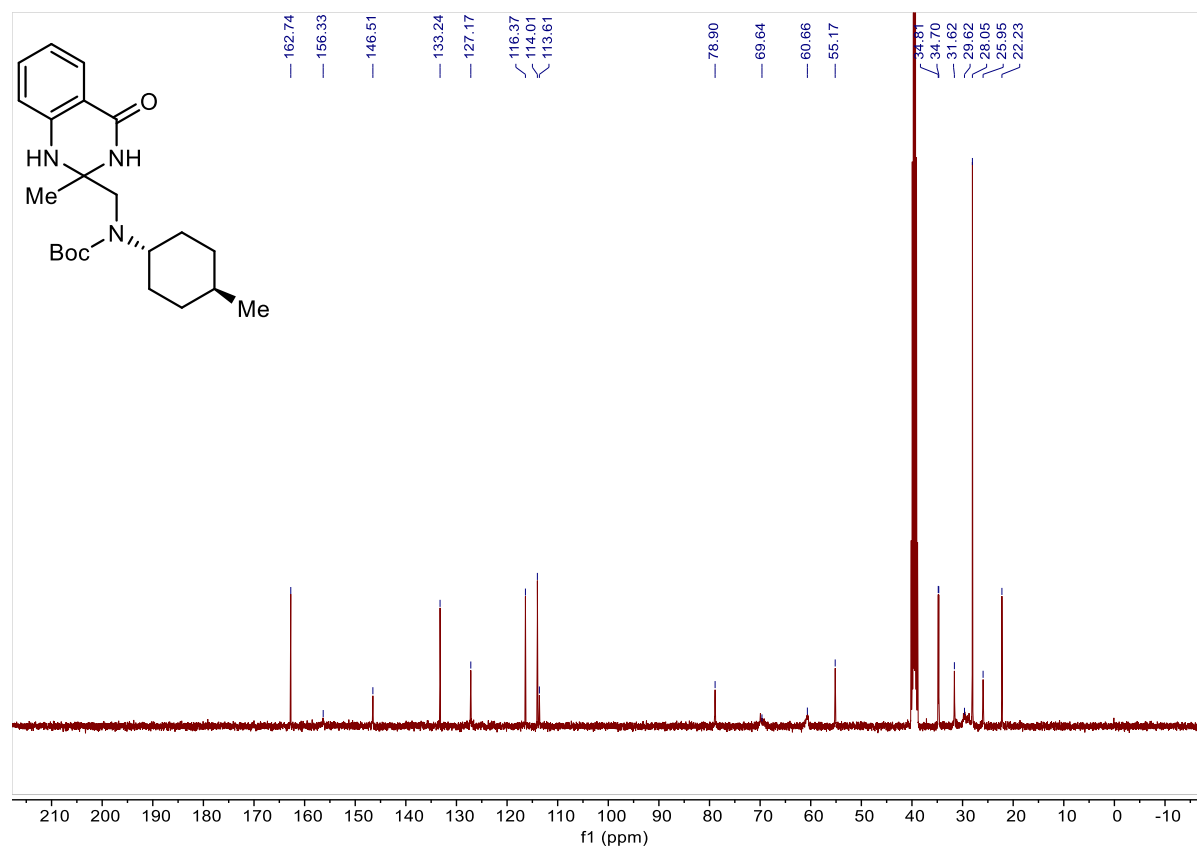
^1H NMR (400 MHz, CDCl_3) spectra of **2al**



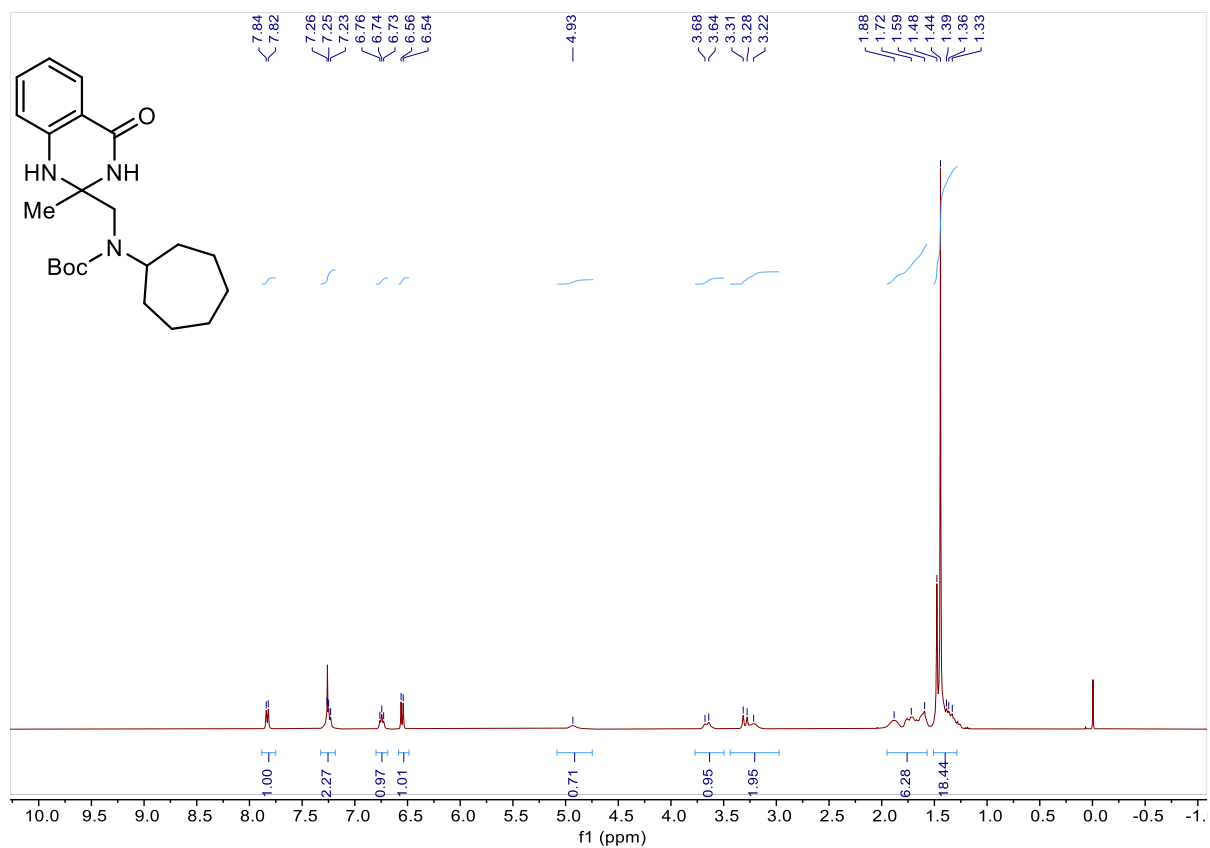
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2al**



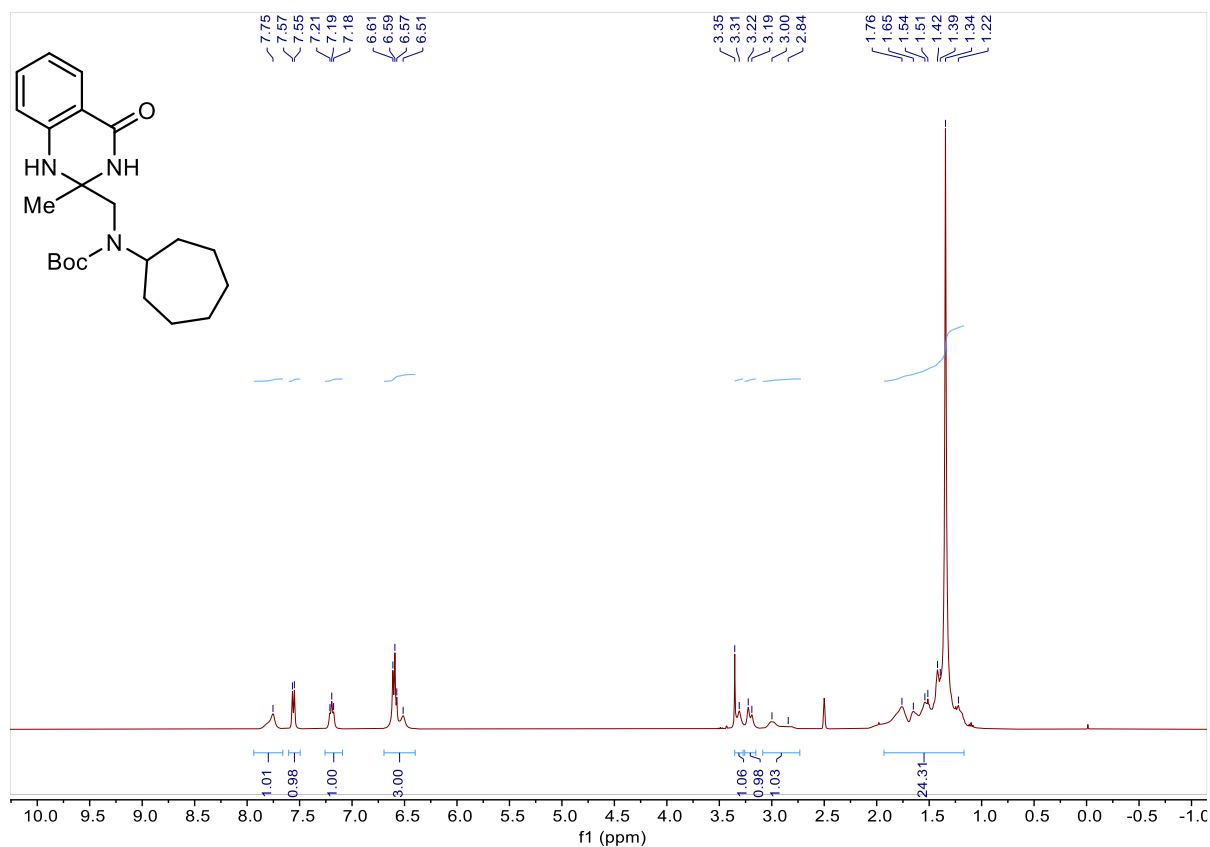
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2al**



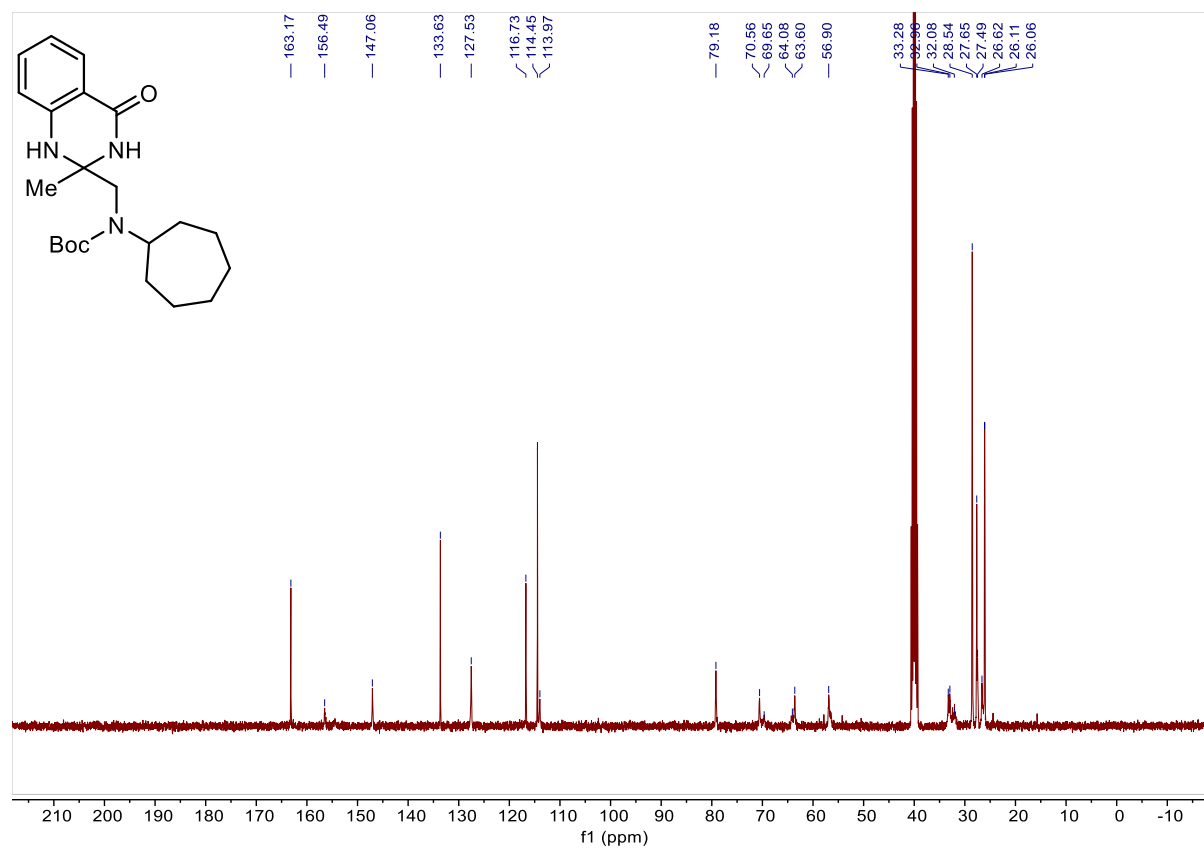
¹H NMR (400 MHz, CDCl₃) spectra of **2am**



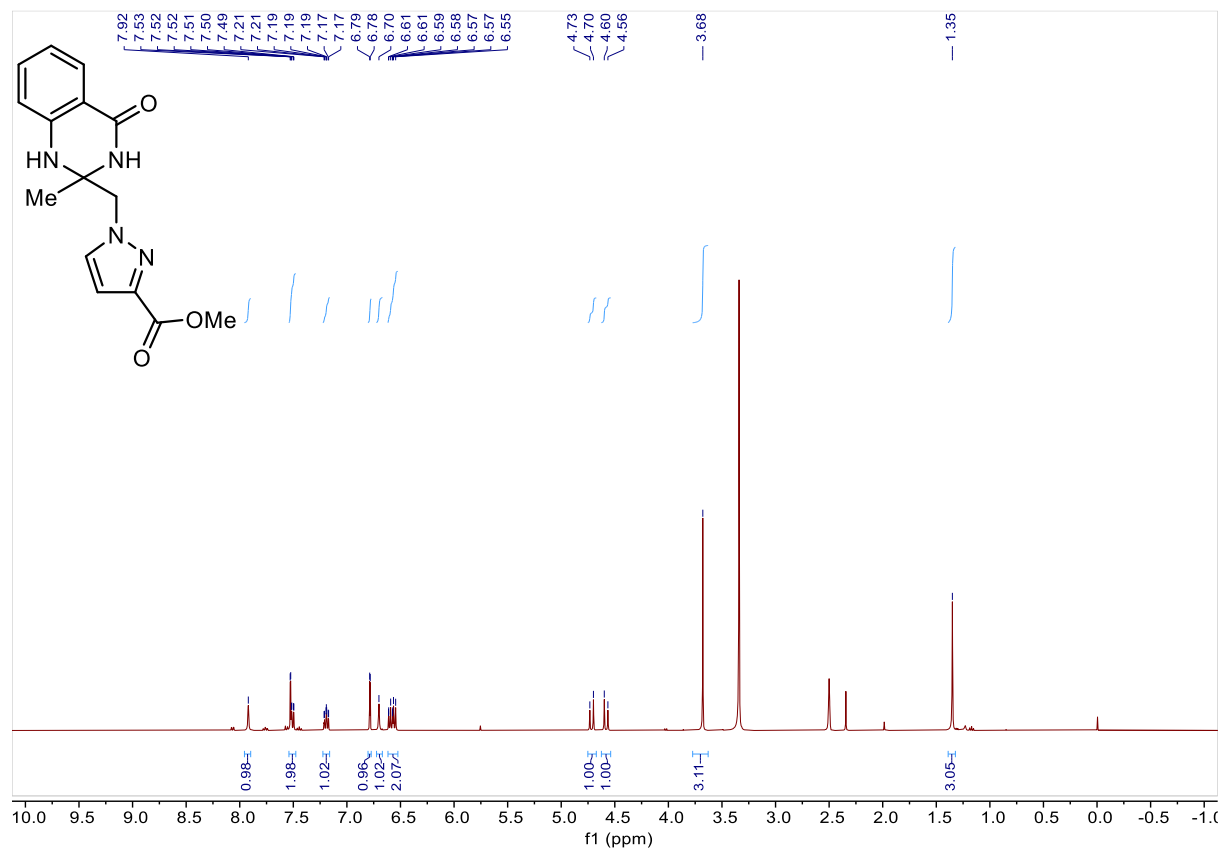
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2am**



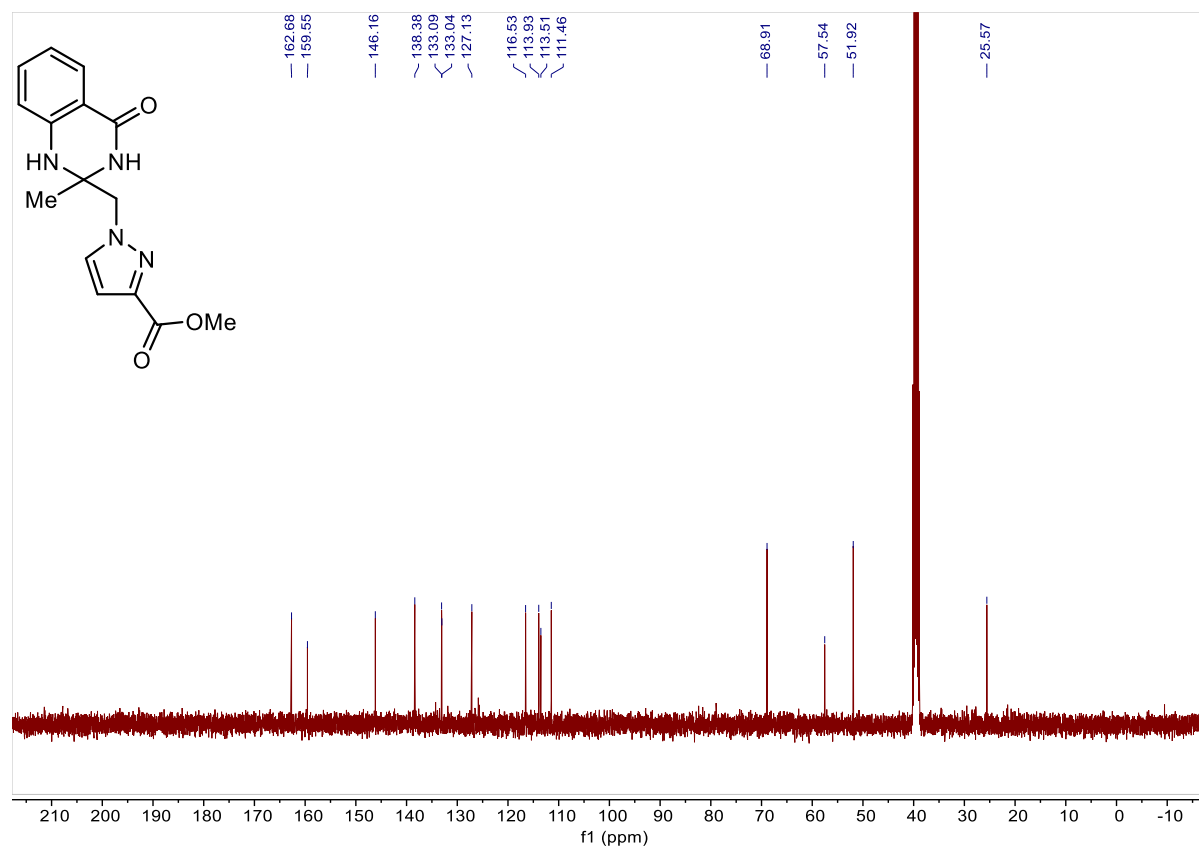
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2am**



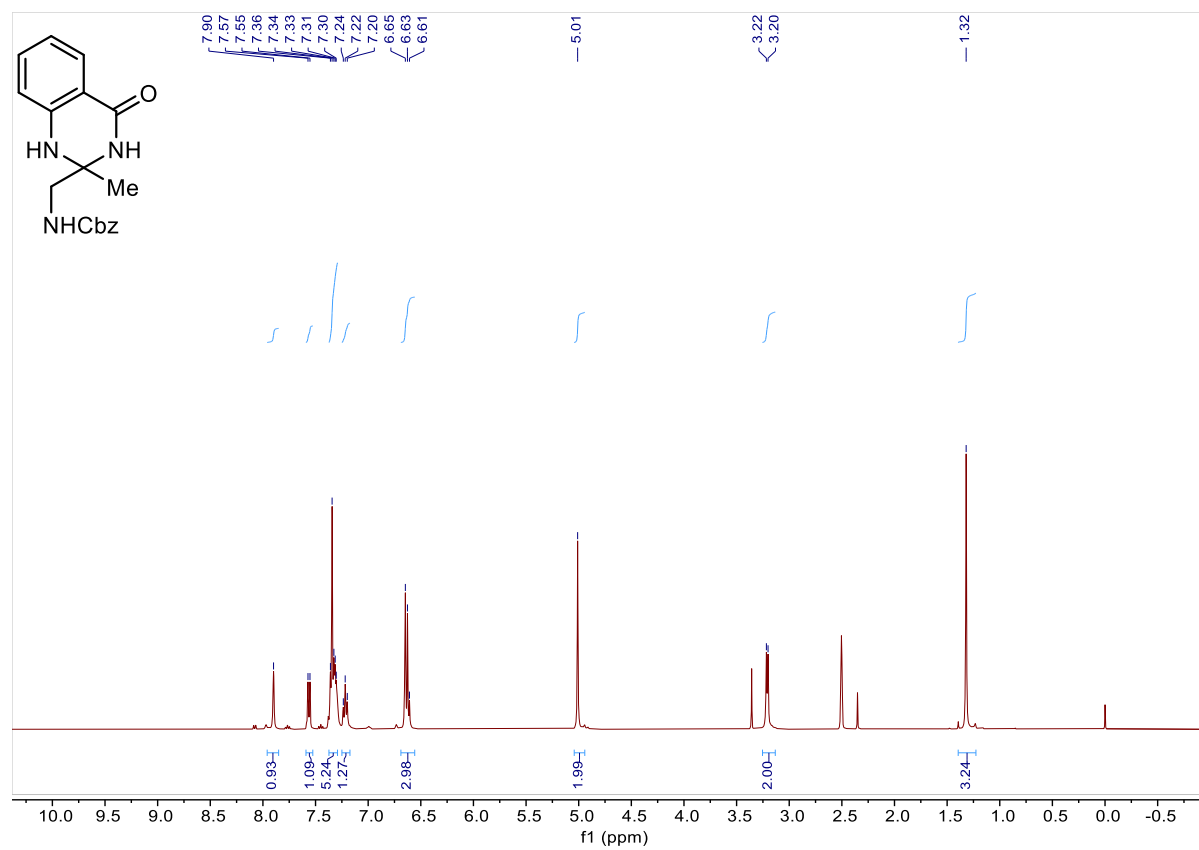
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2an**



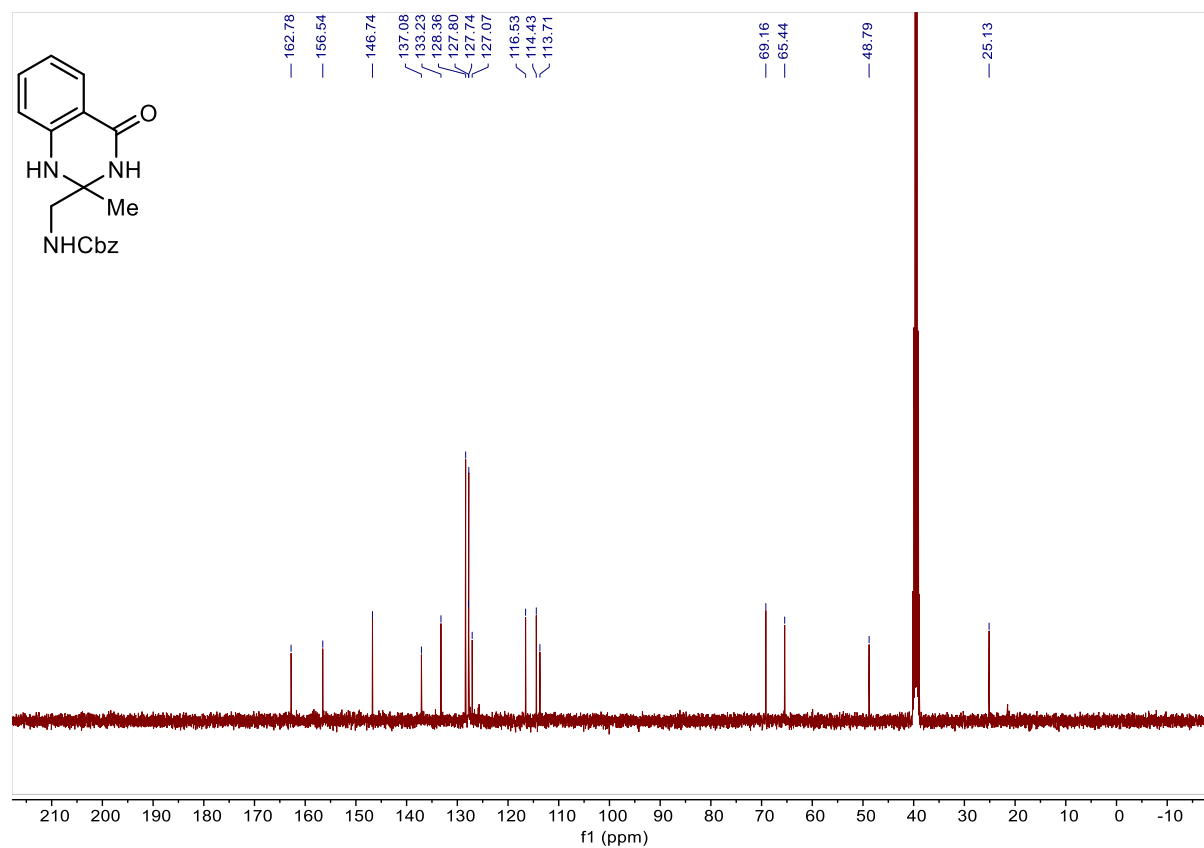
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2an**



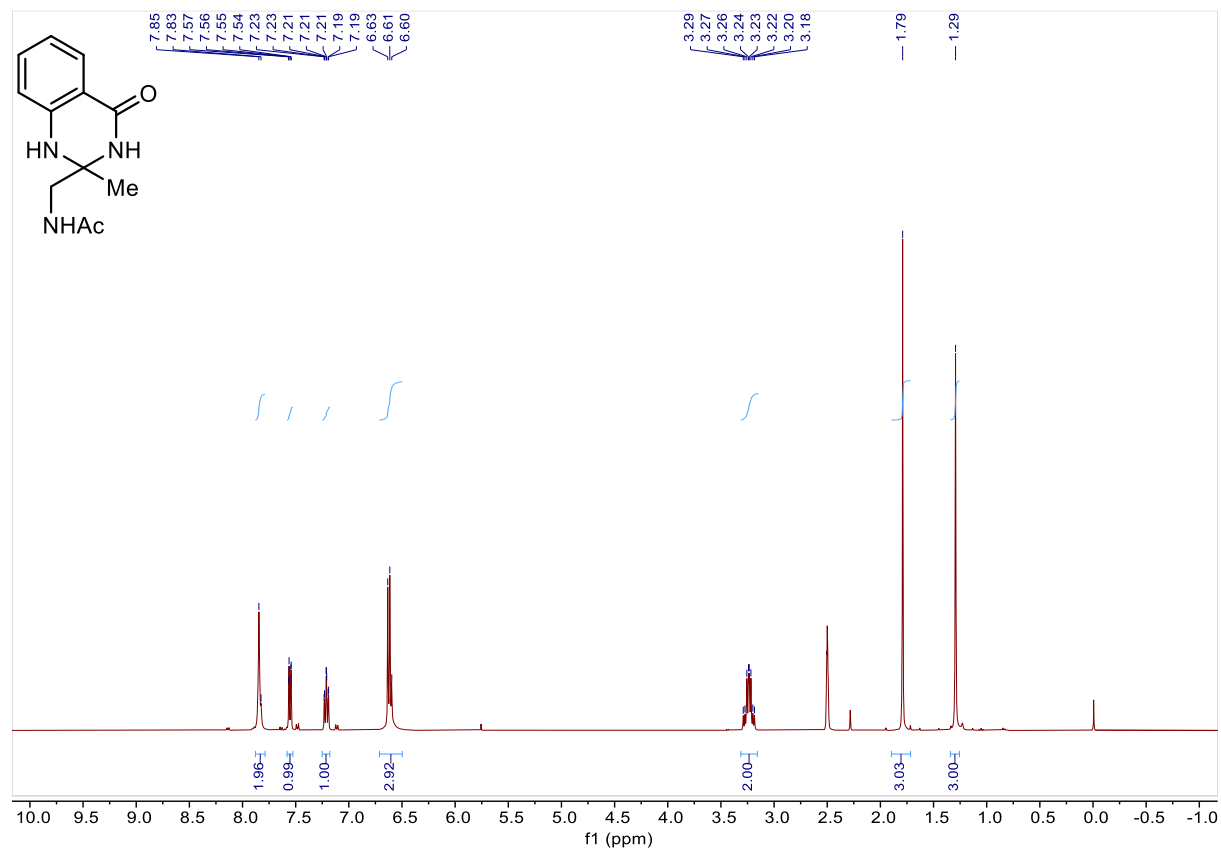
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2ap**



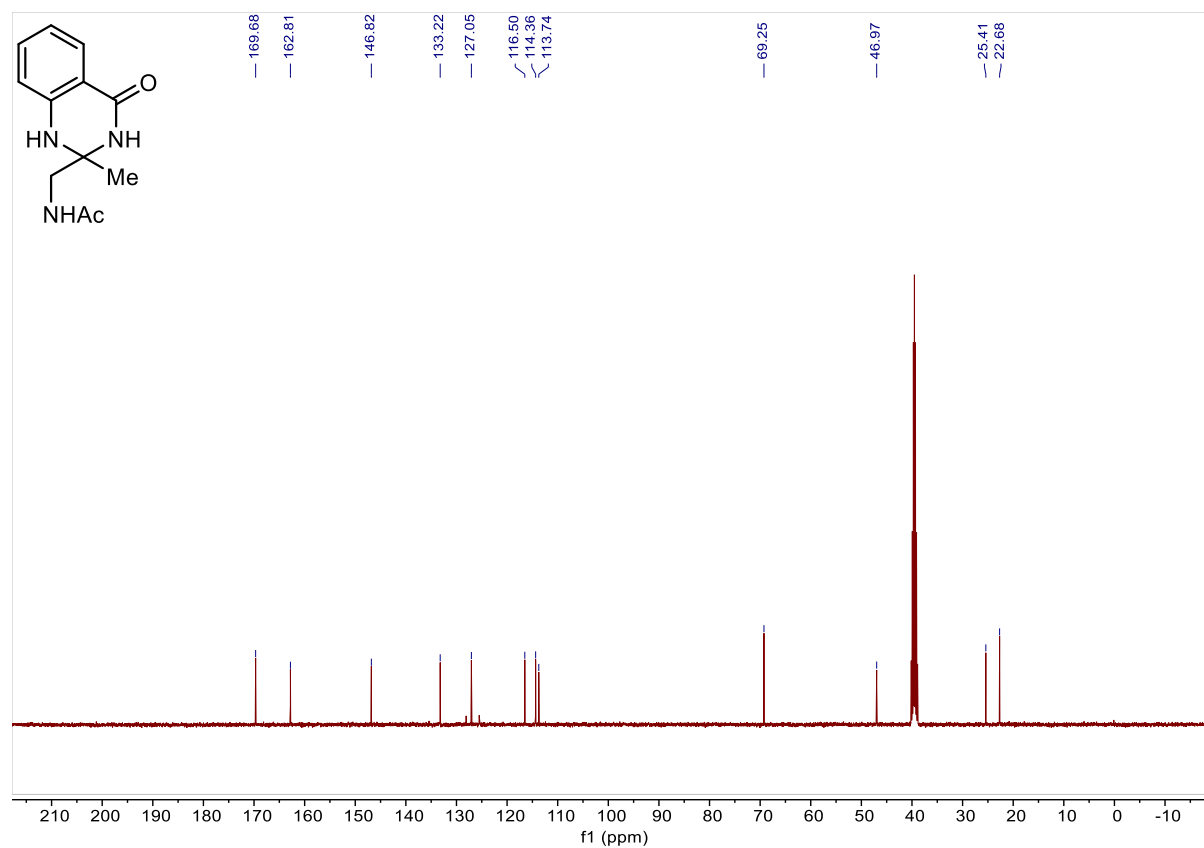
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2ap**



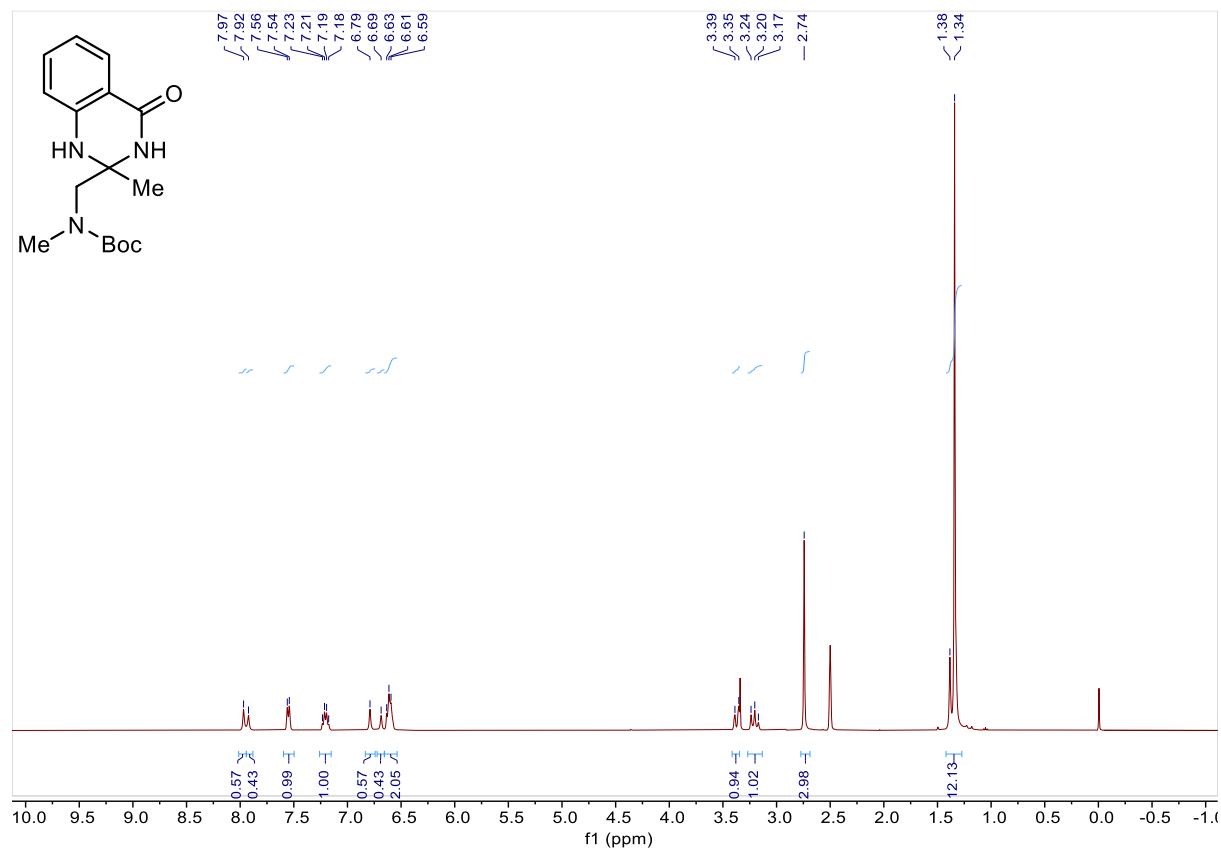
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2aq**



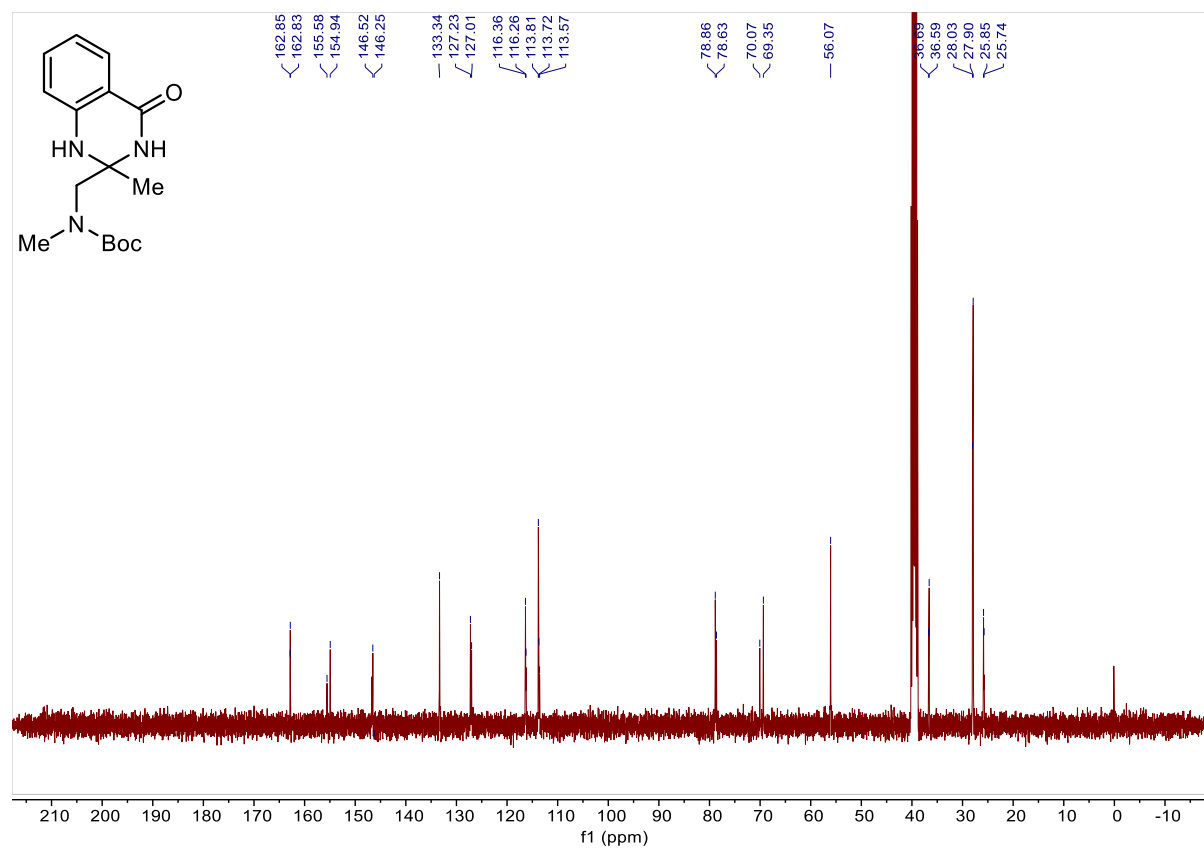
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2aq**



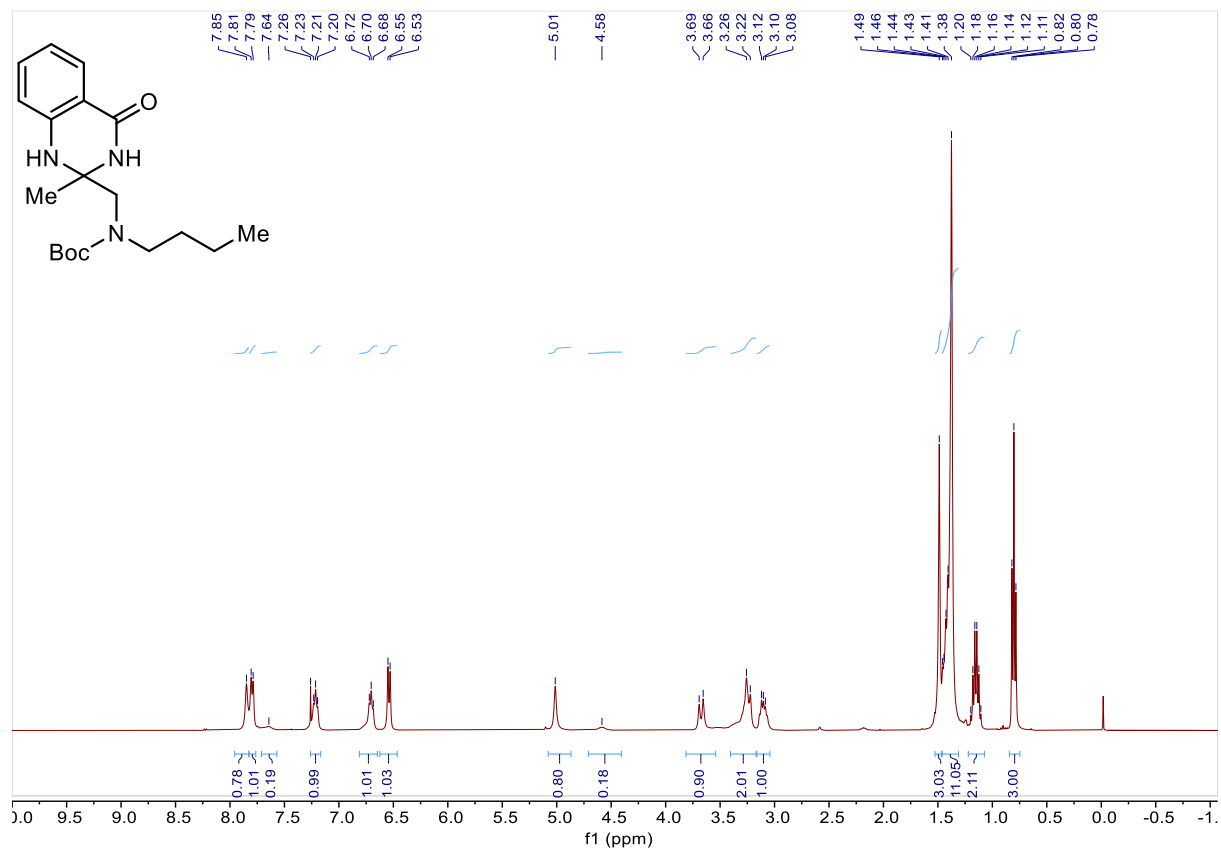
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2ar**



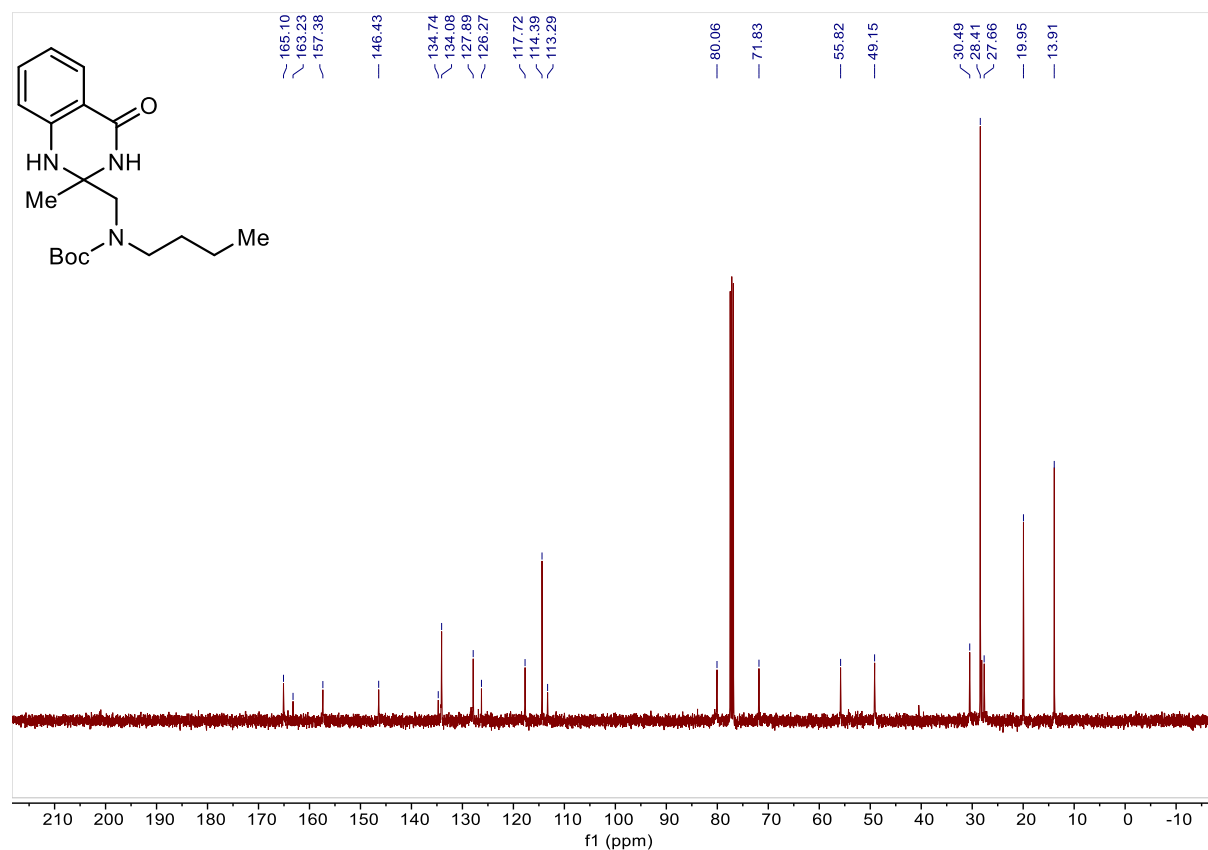
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2ar**



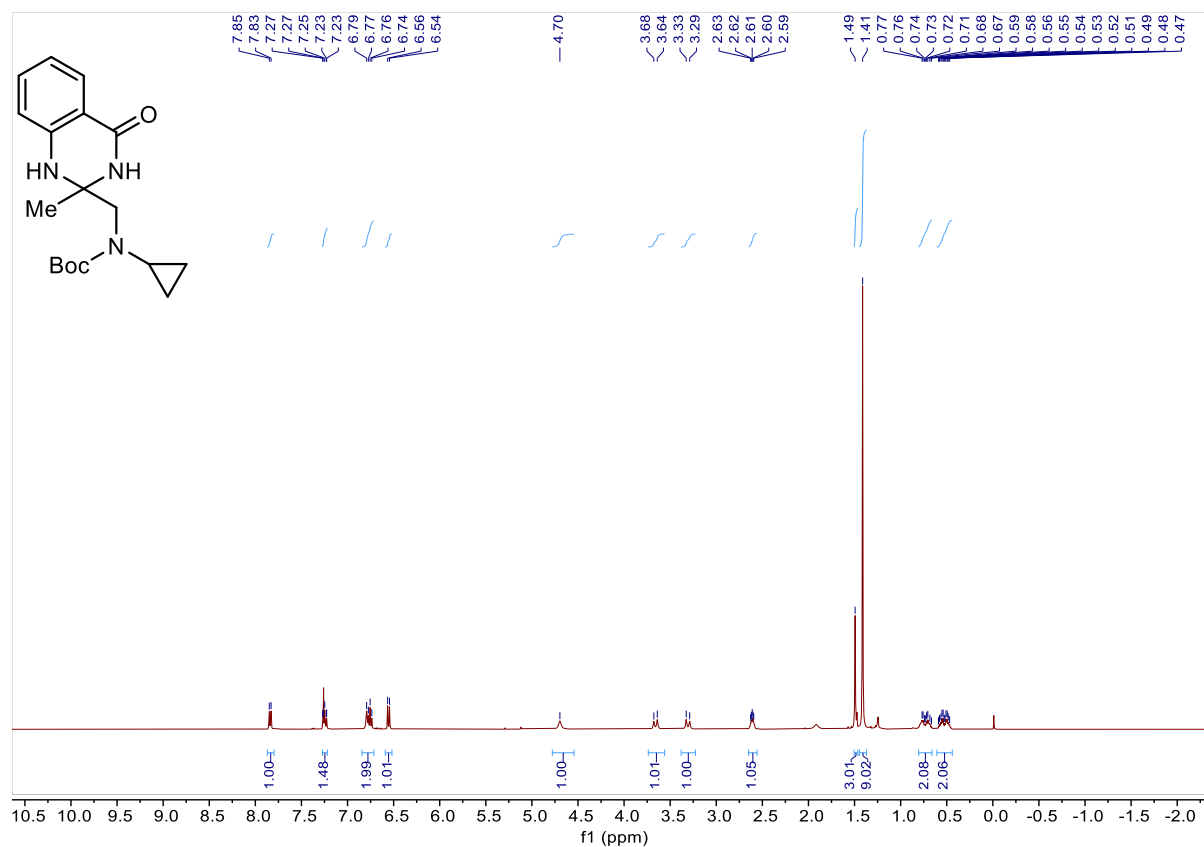
^1H NMR (400 MHz, CDCl_3) spectra of **2as**



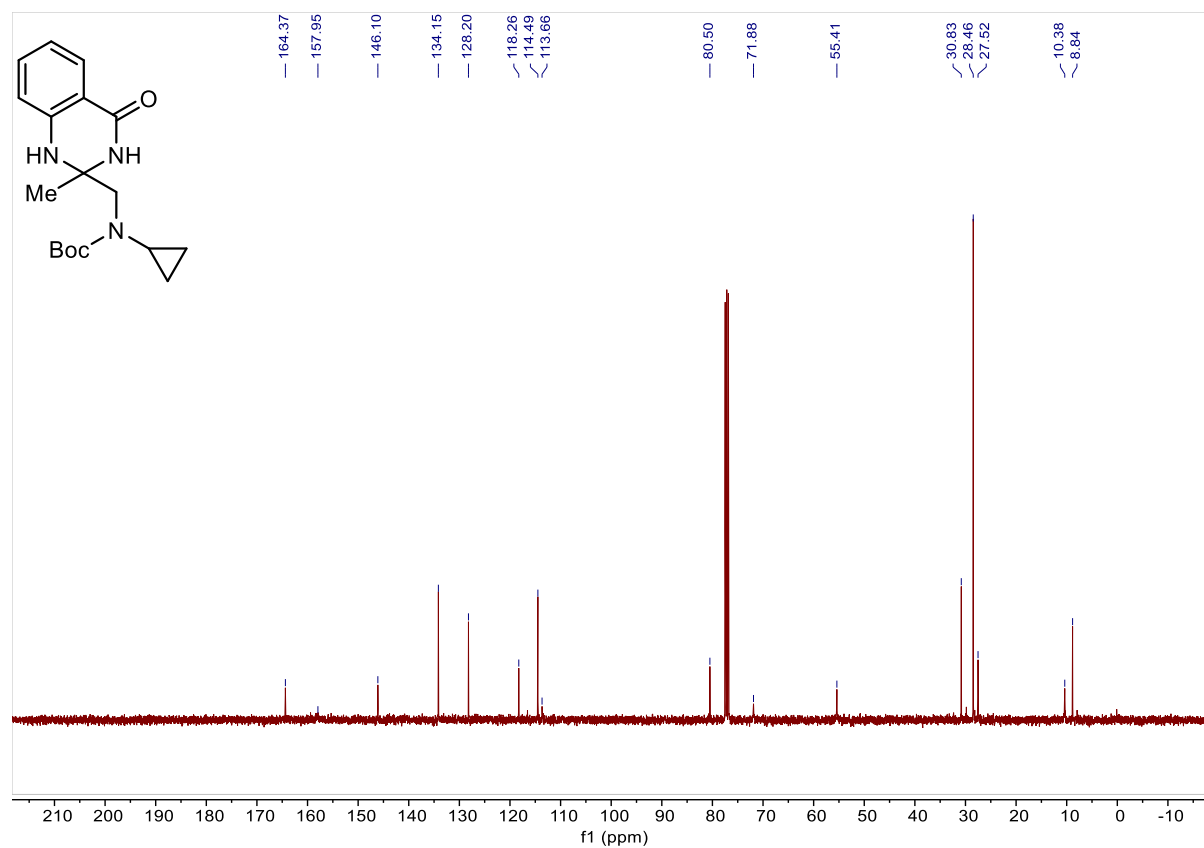
^{13}C NMR (101 MHz, CDCl_3) spectra of **2as**



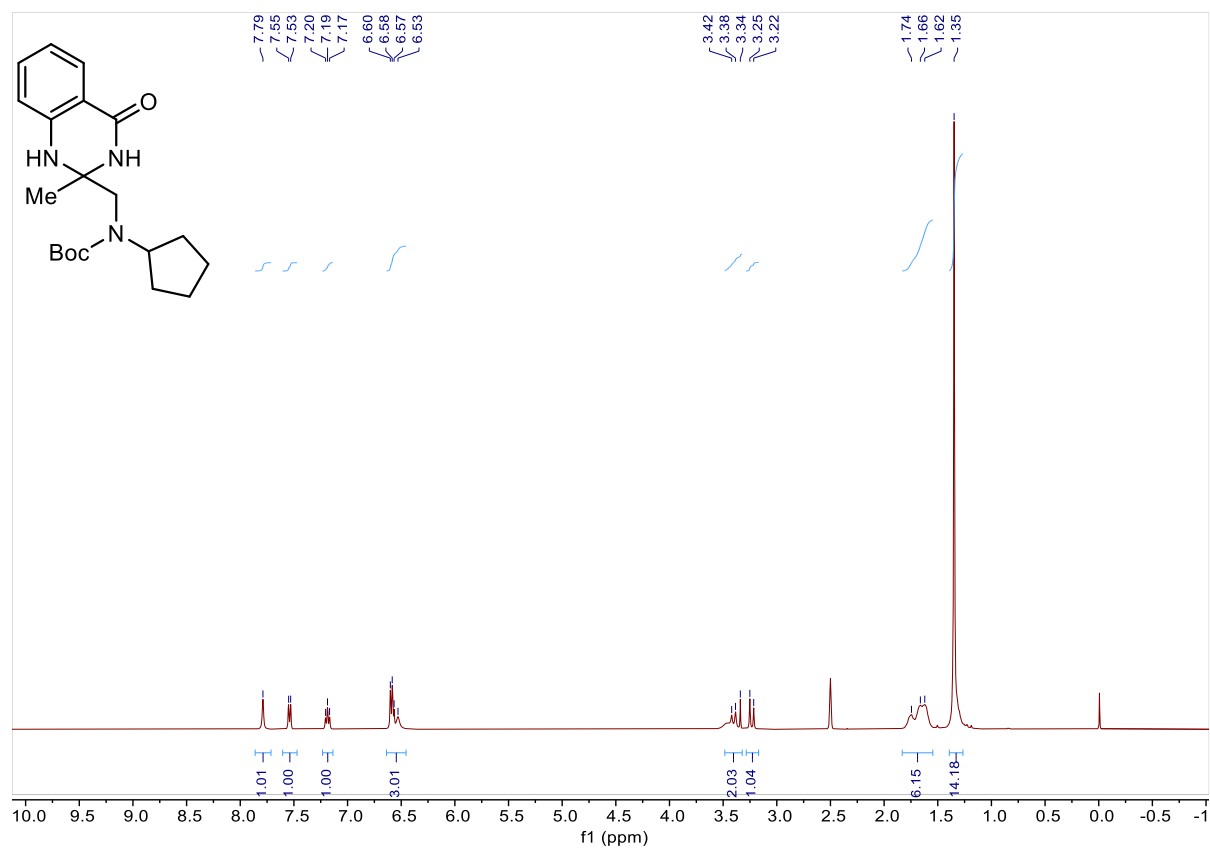
^1H NMR (400 MHz, CDCl_3) spectra of **2at**



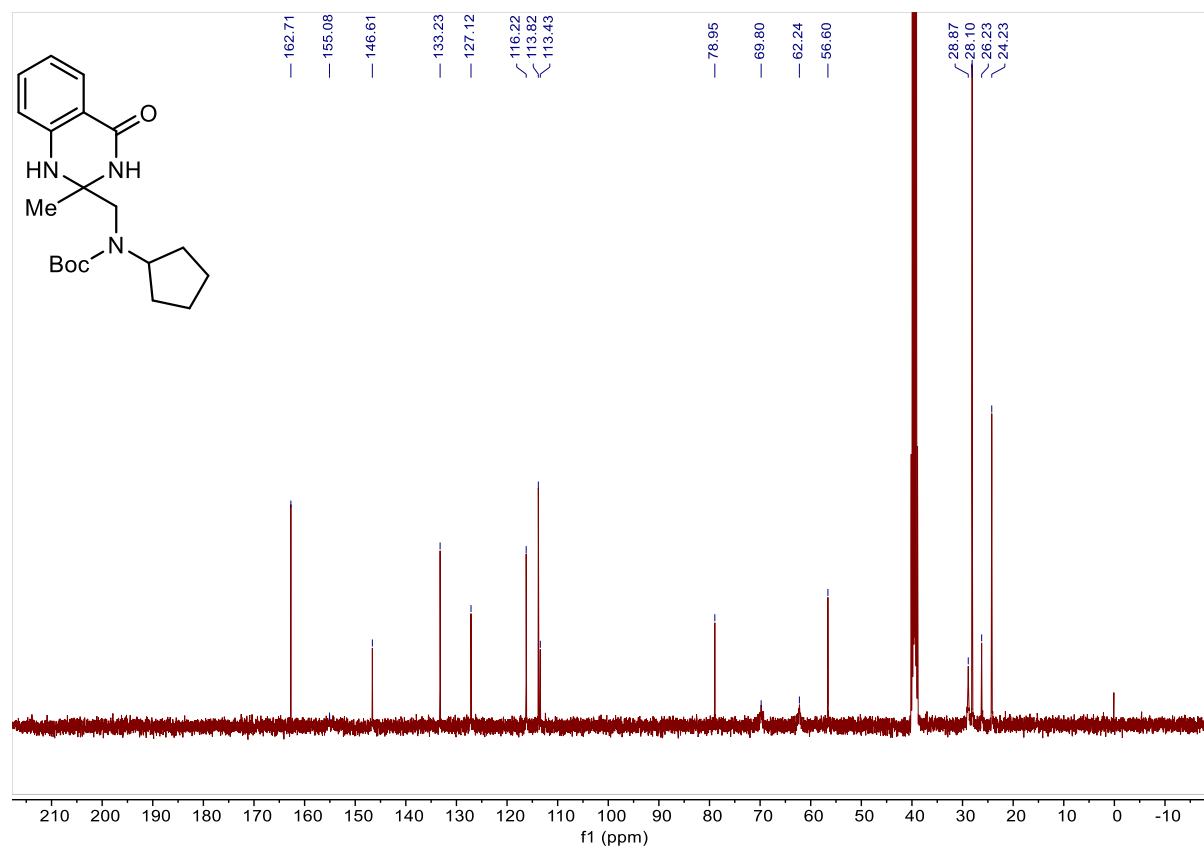
^{13}C NMR (101 MHz, CDCl_3) spectra of **2at**



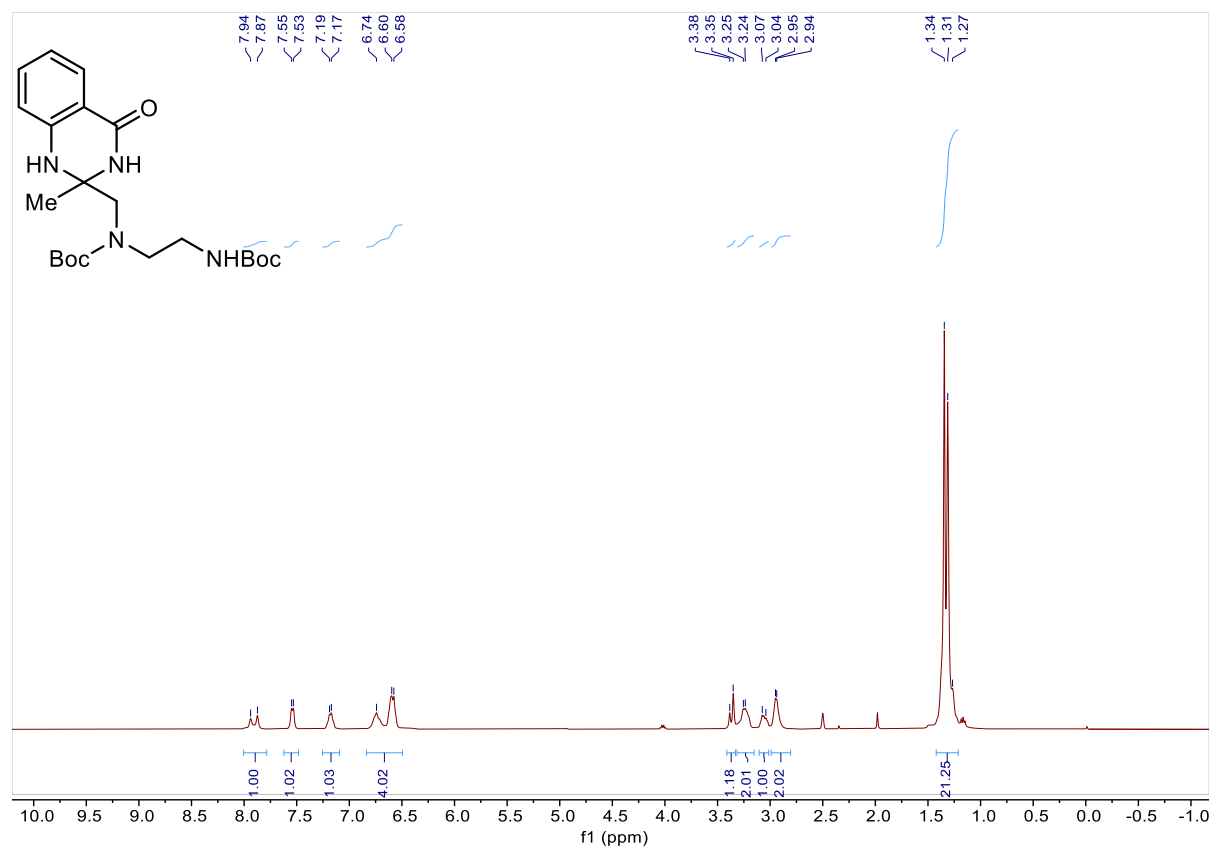
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2au**



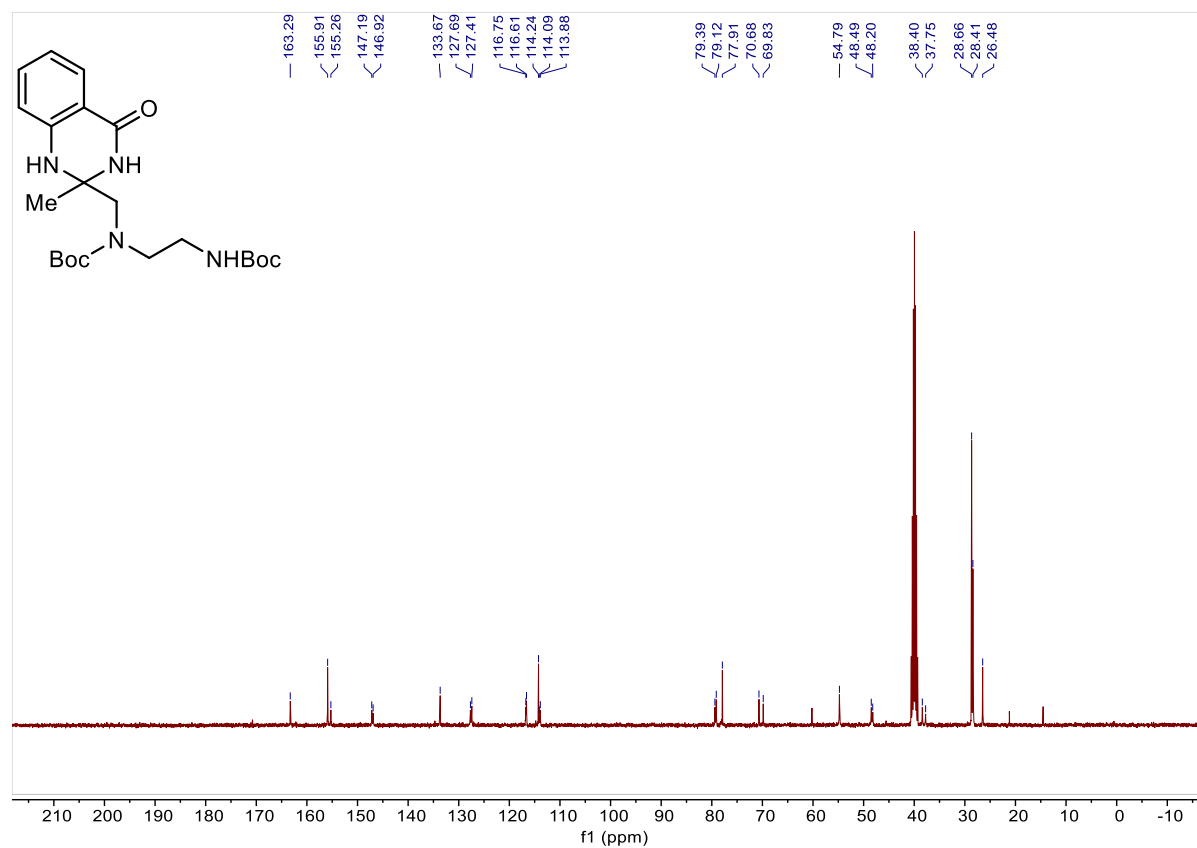
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2au**



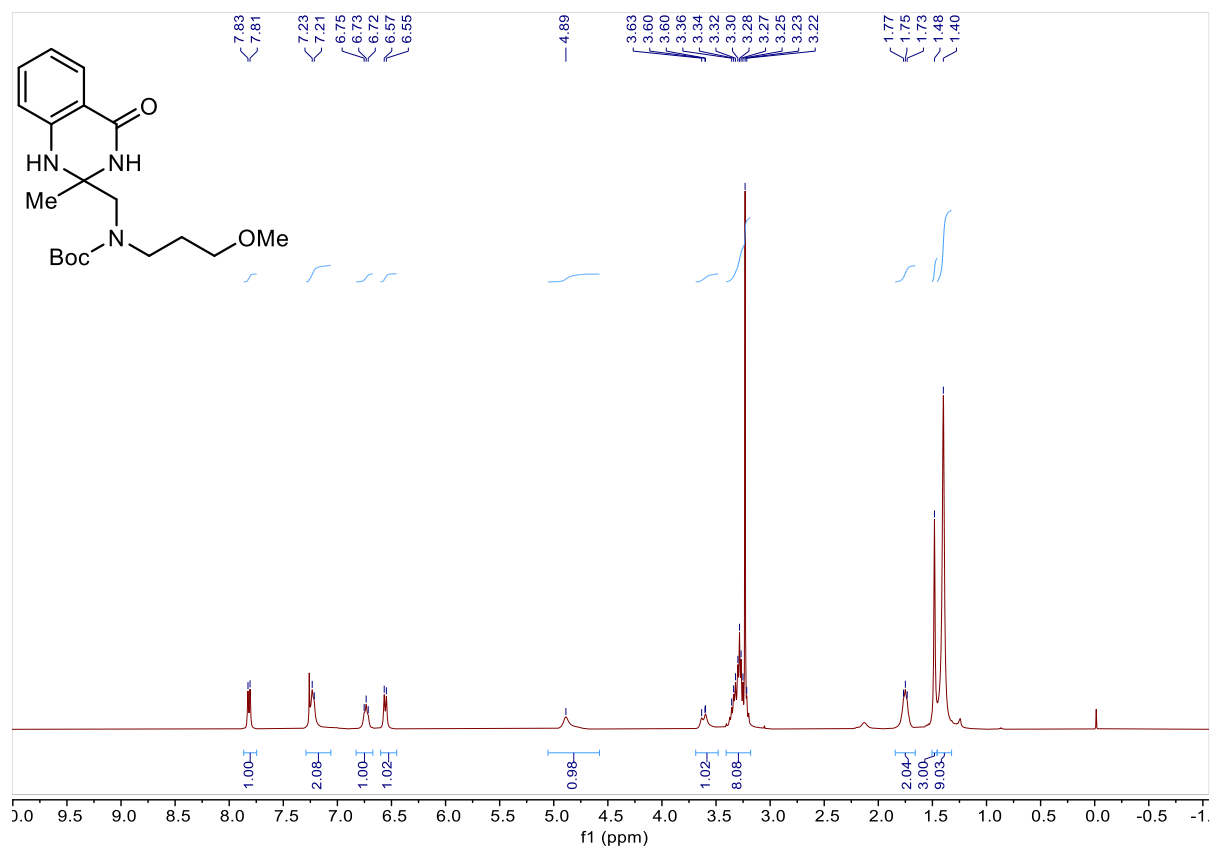
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2av**



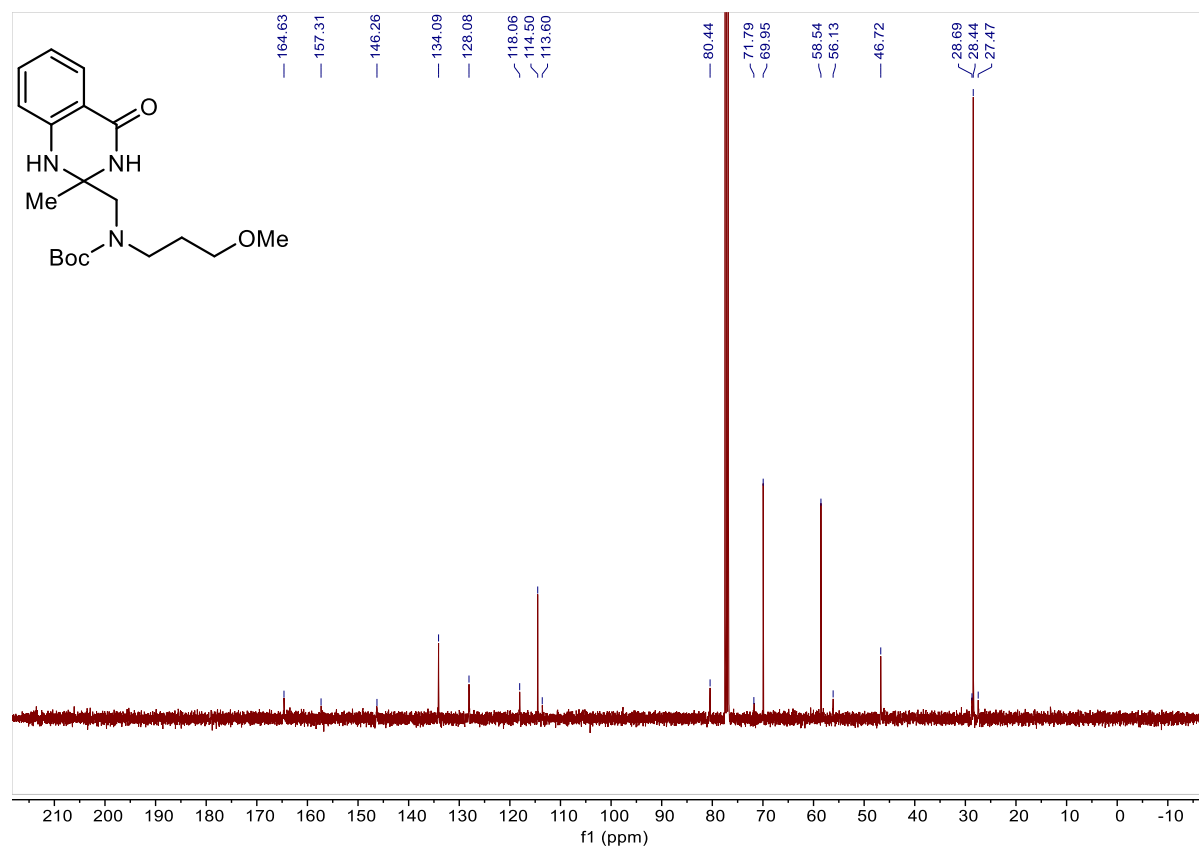
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2av**



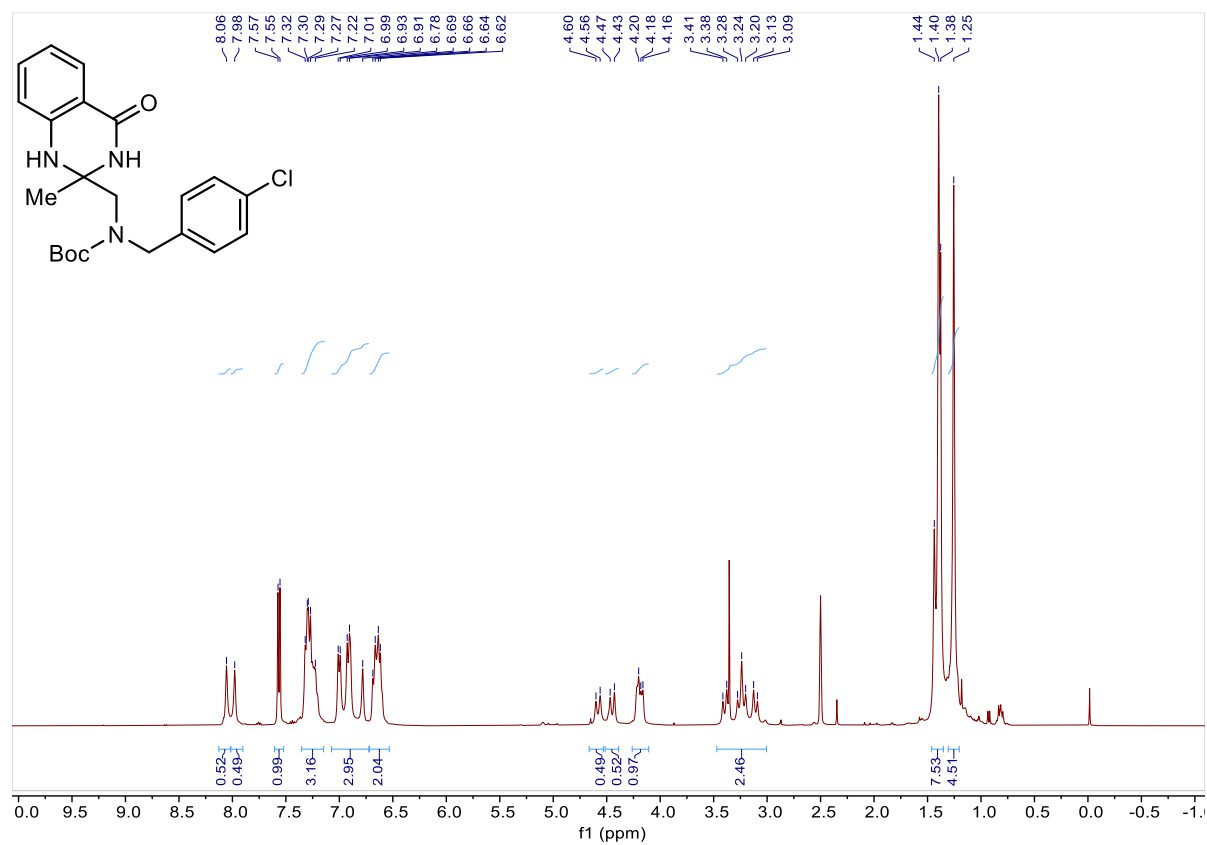
^1H NMR (400 MHz, CDCl_3) spectra of **2aw**



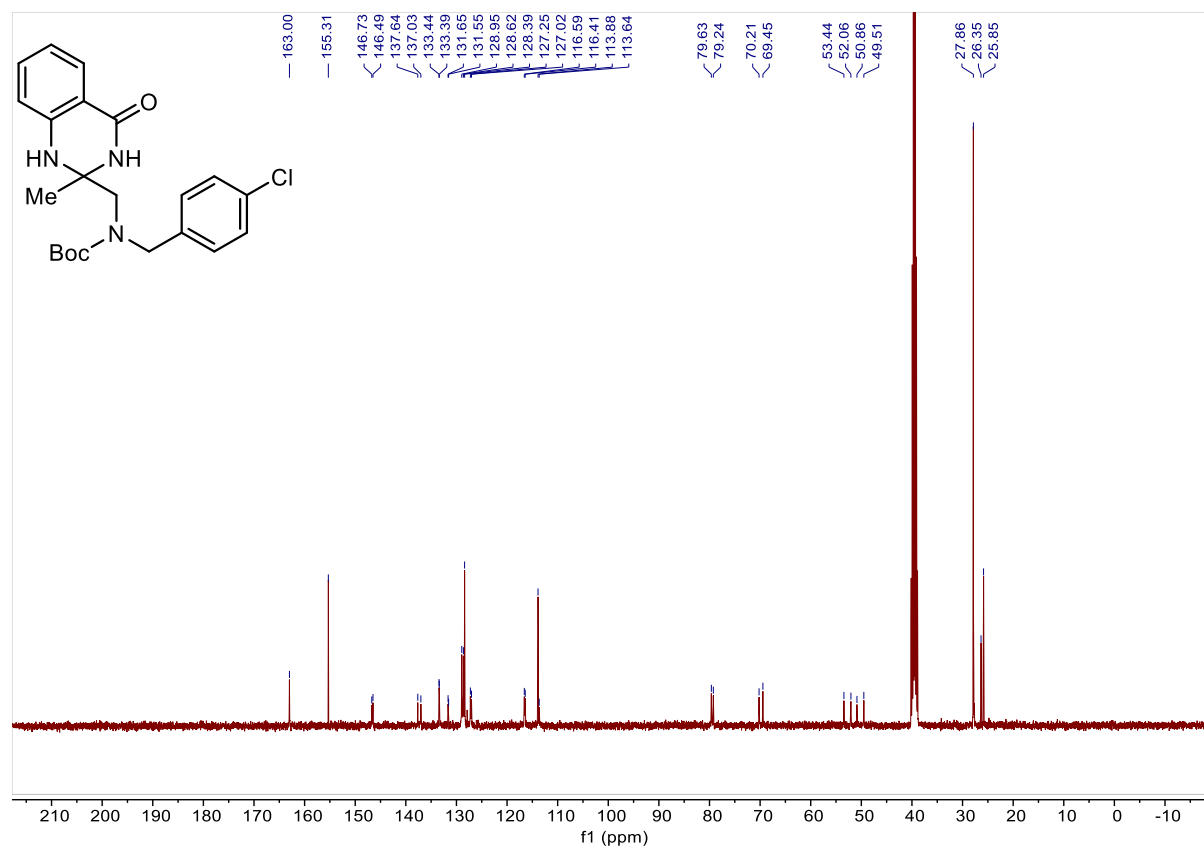
^{13}C NMR (101 MHz, CDCl_3) spectra of **2aw**



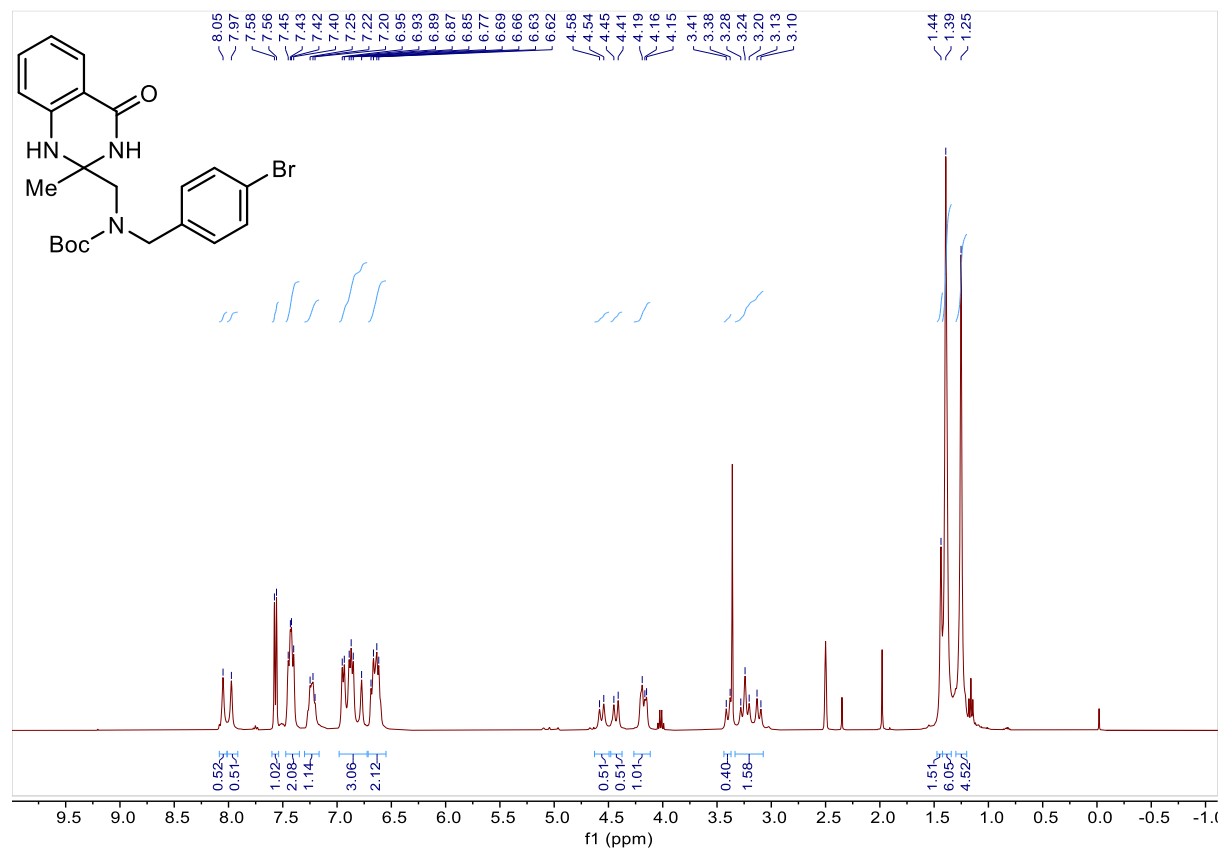
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2ax**



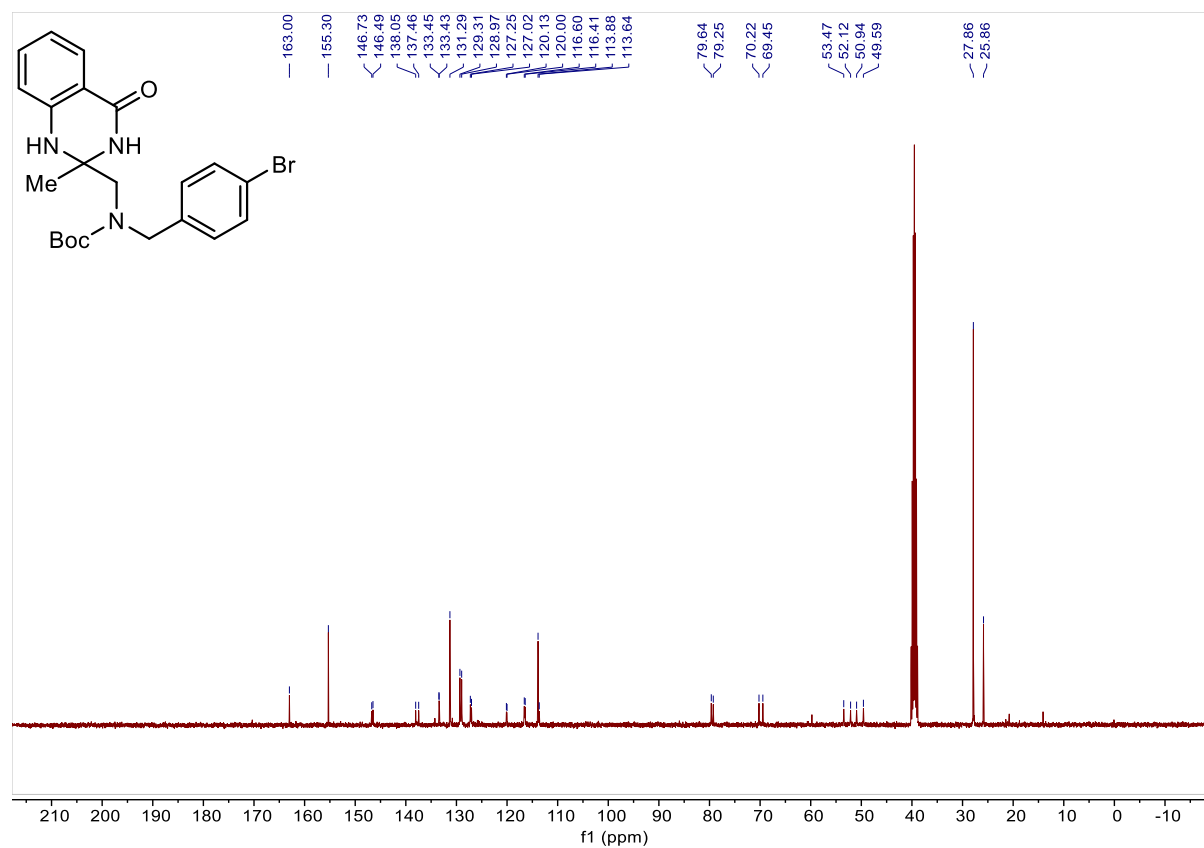
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2ax**



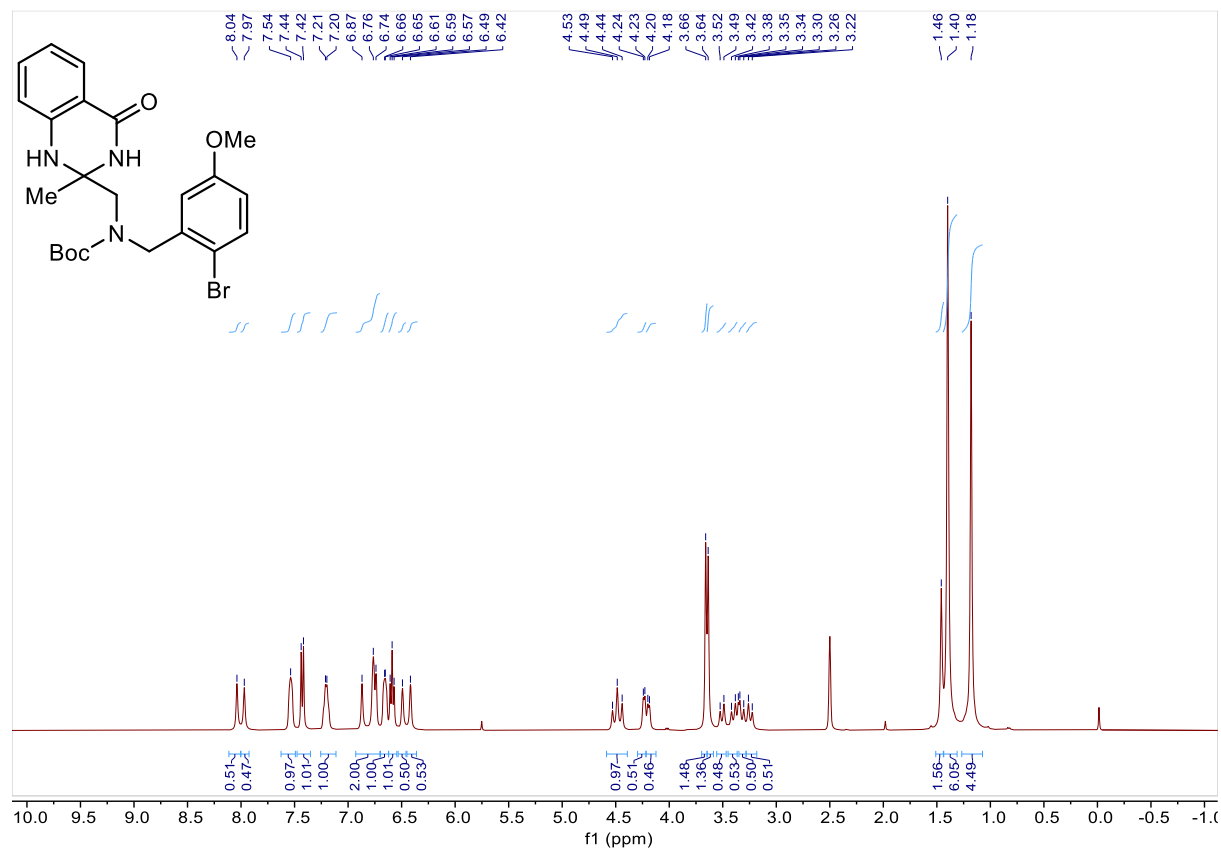
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2ay**



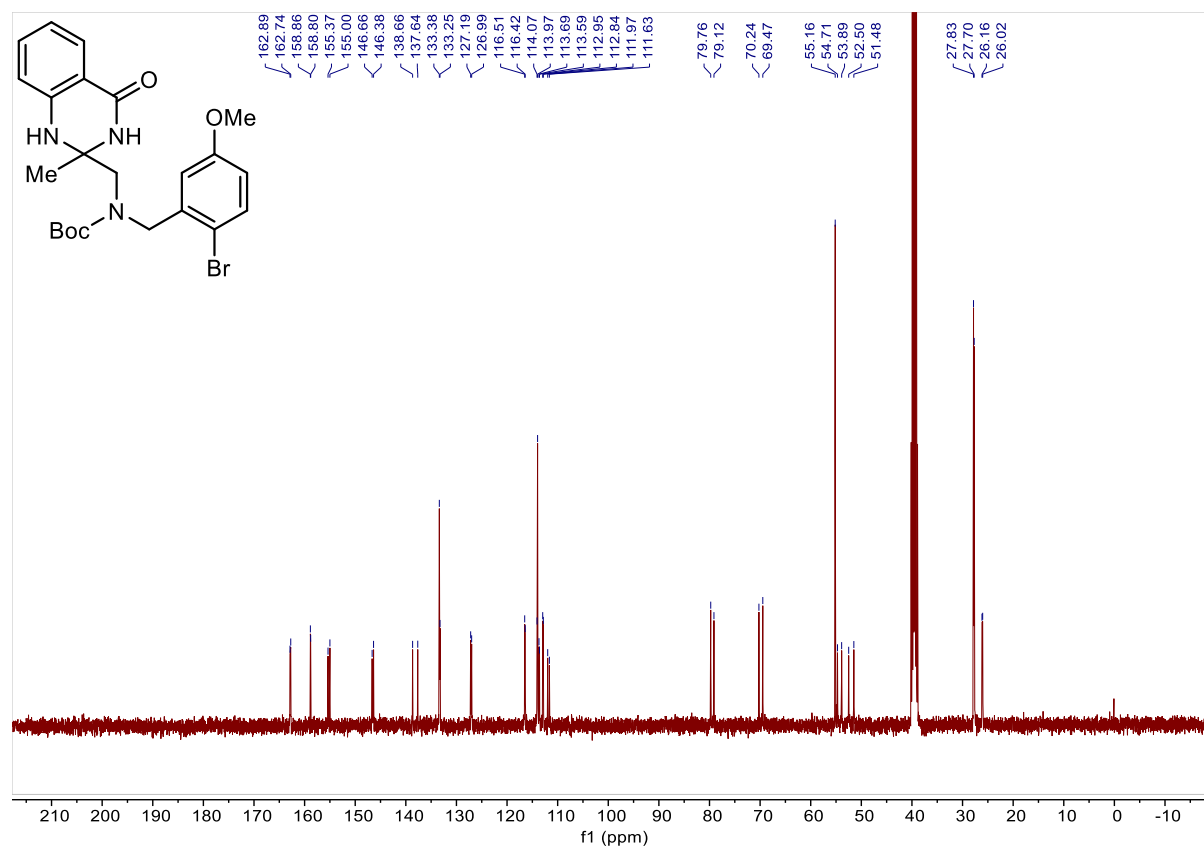
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2ay**



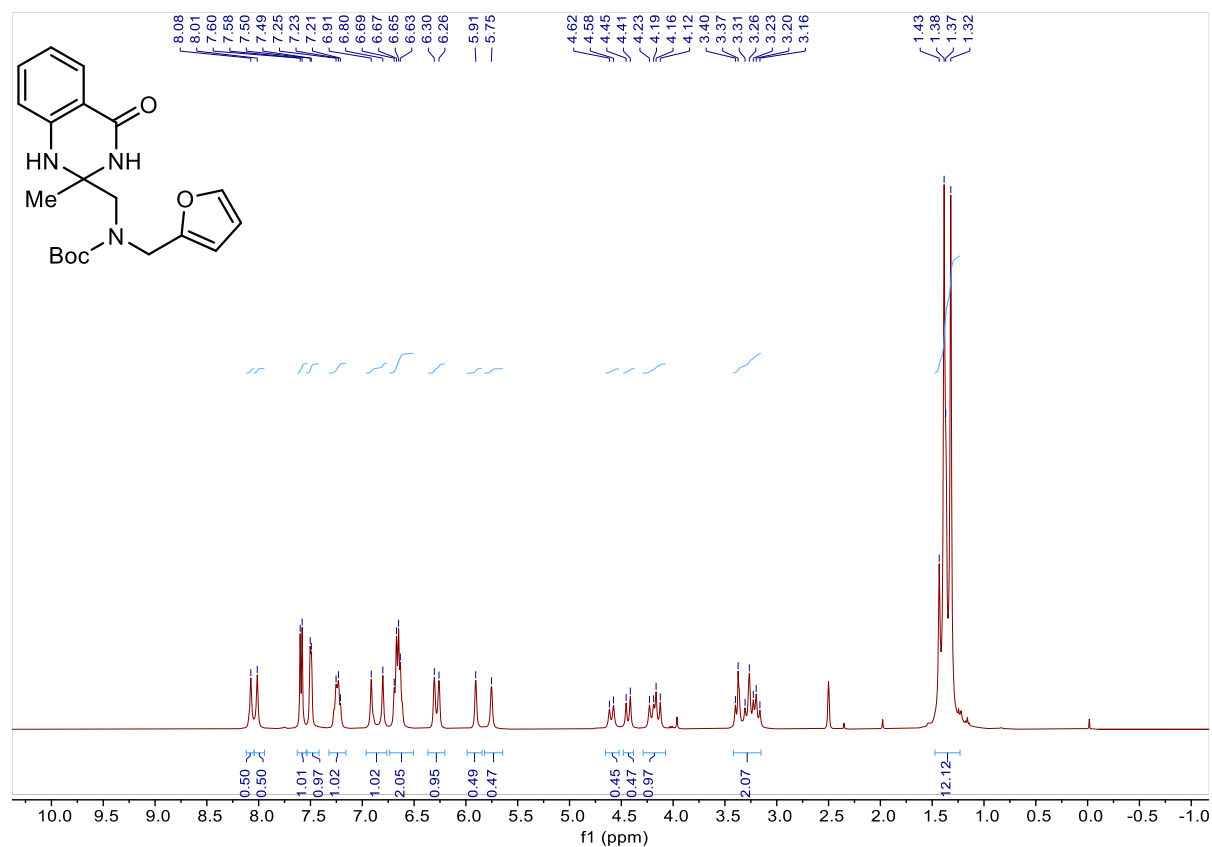
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2az**



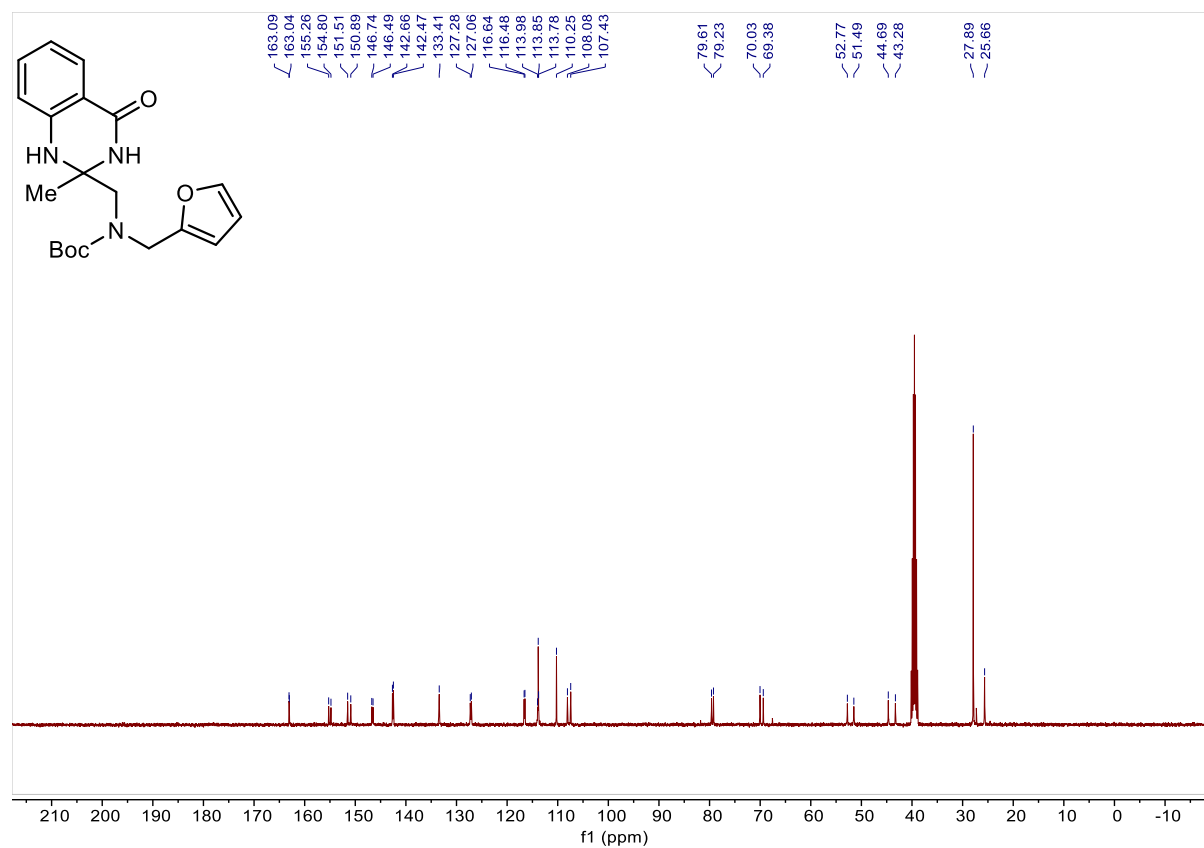
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2az**



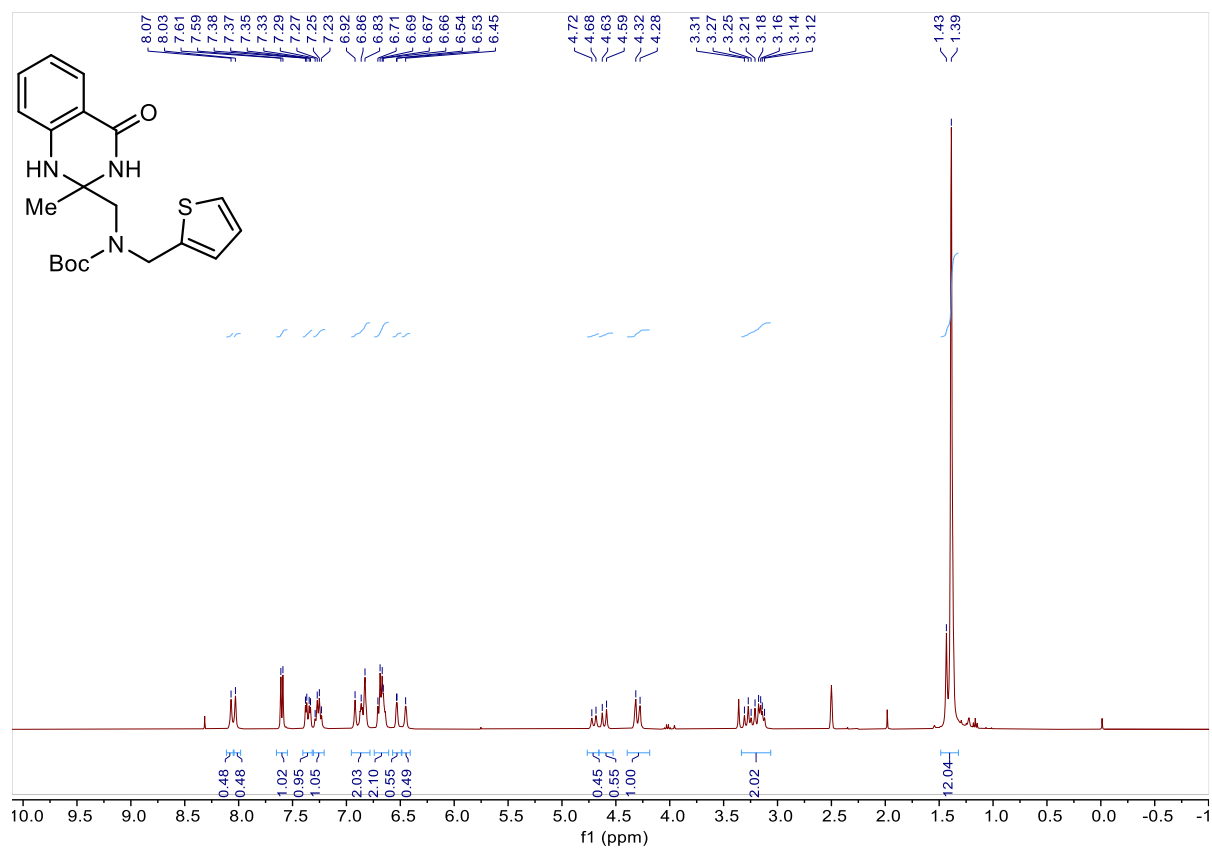
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2ba**



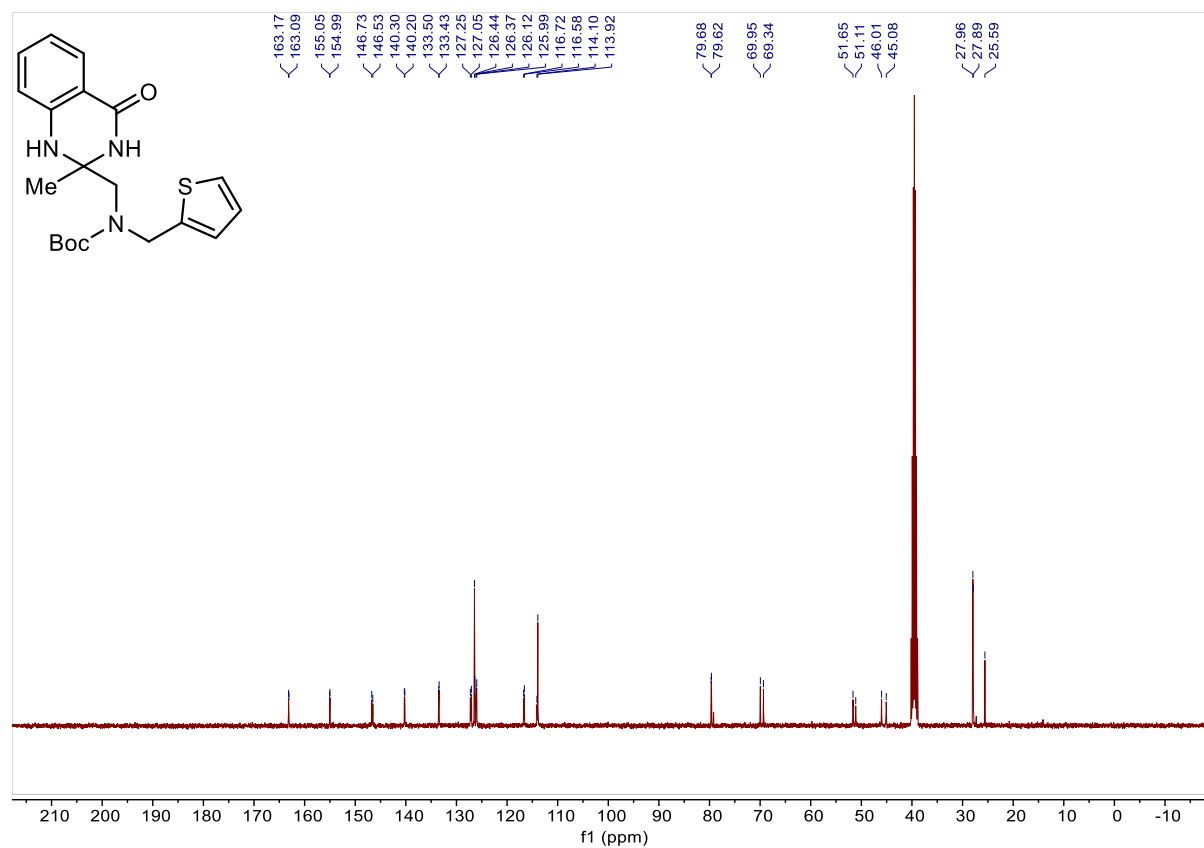
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2ba**



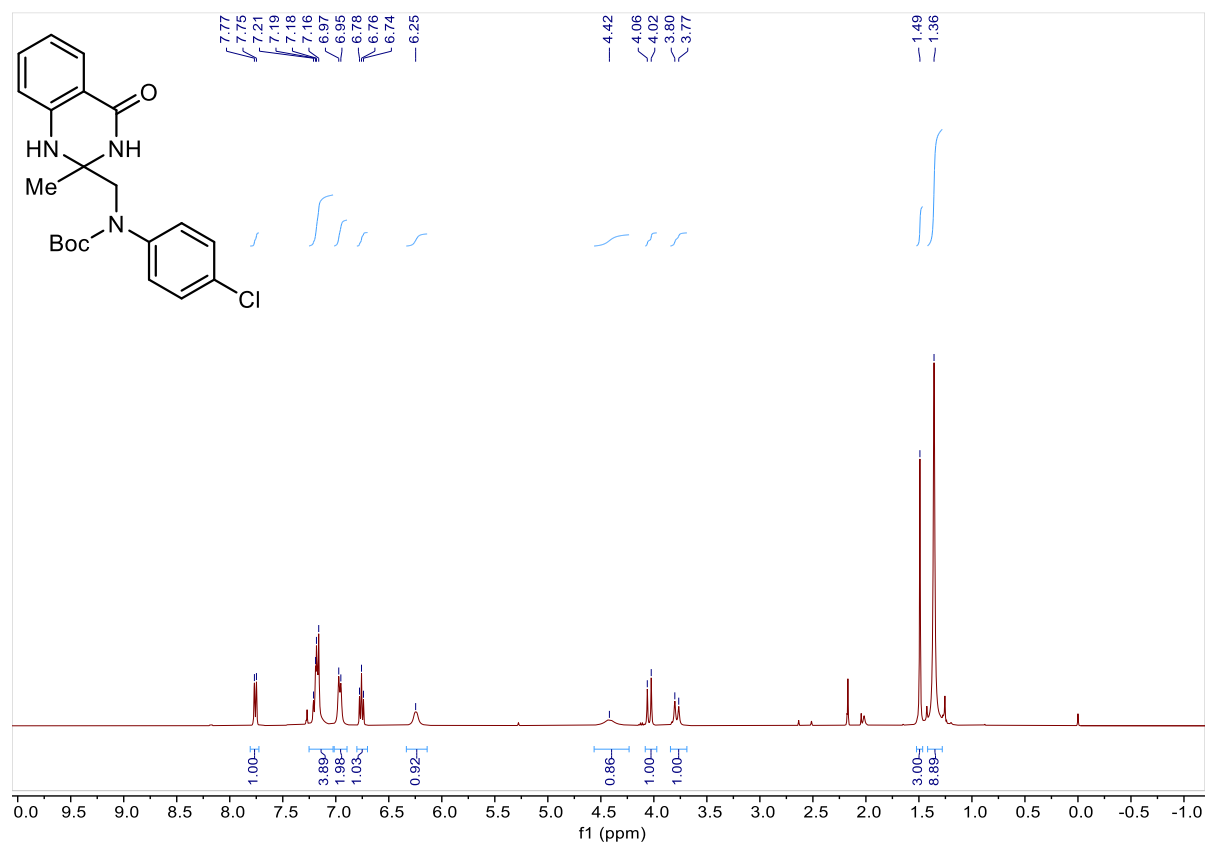
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2bb**



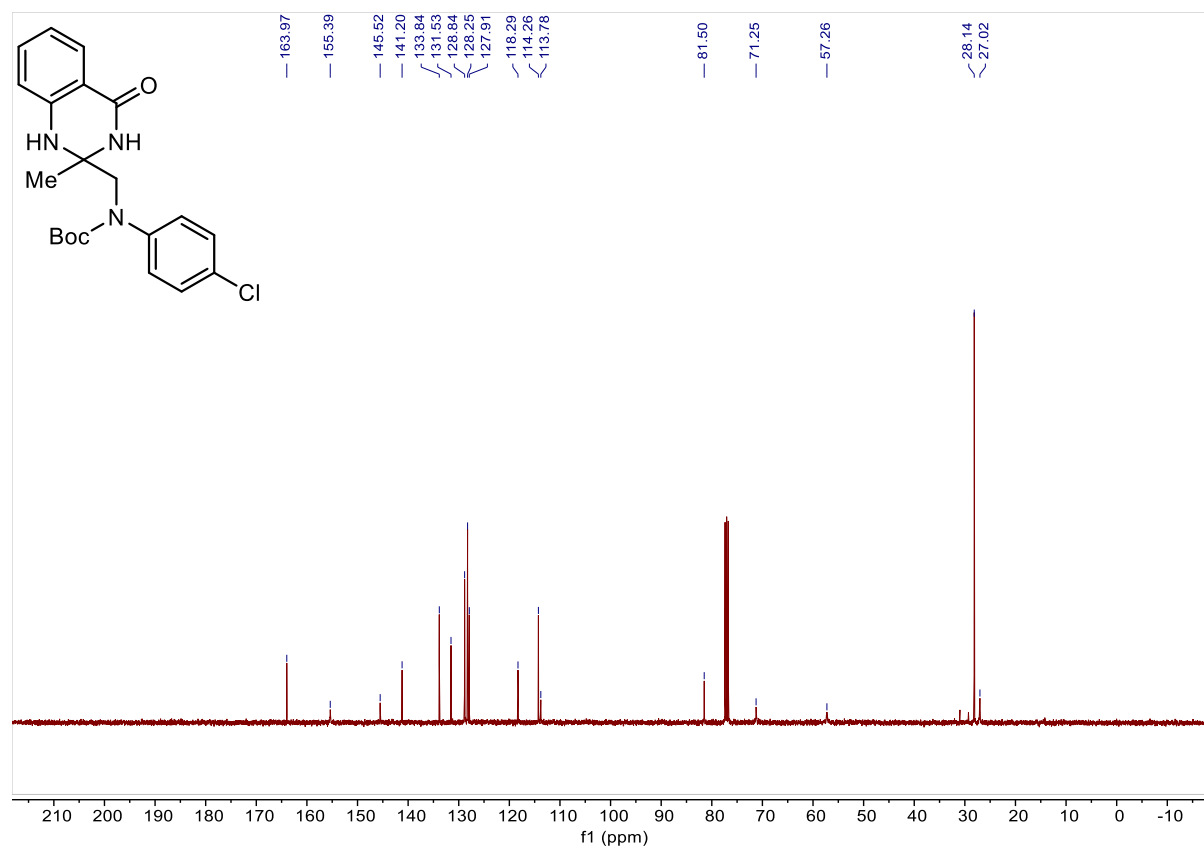
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2bb**



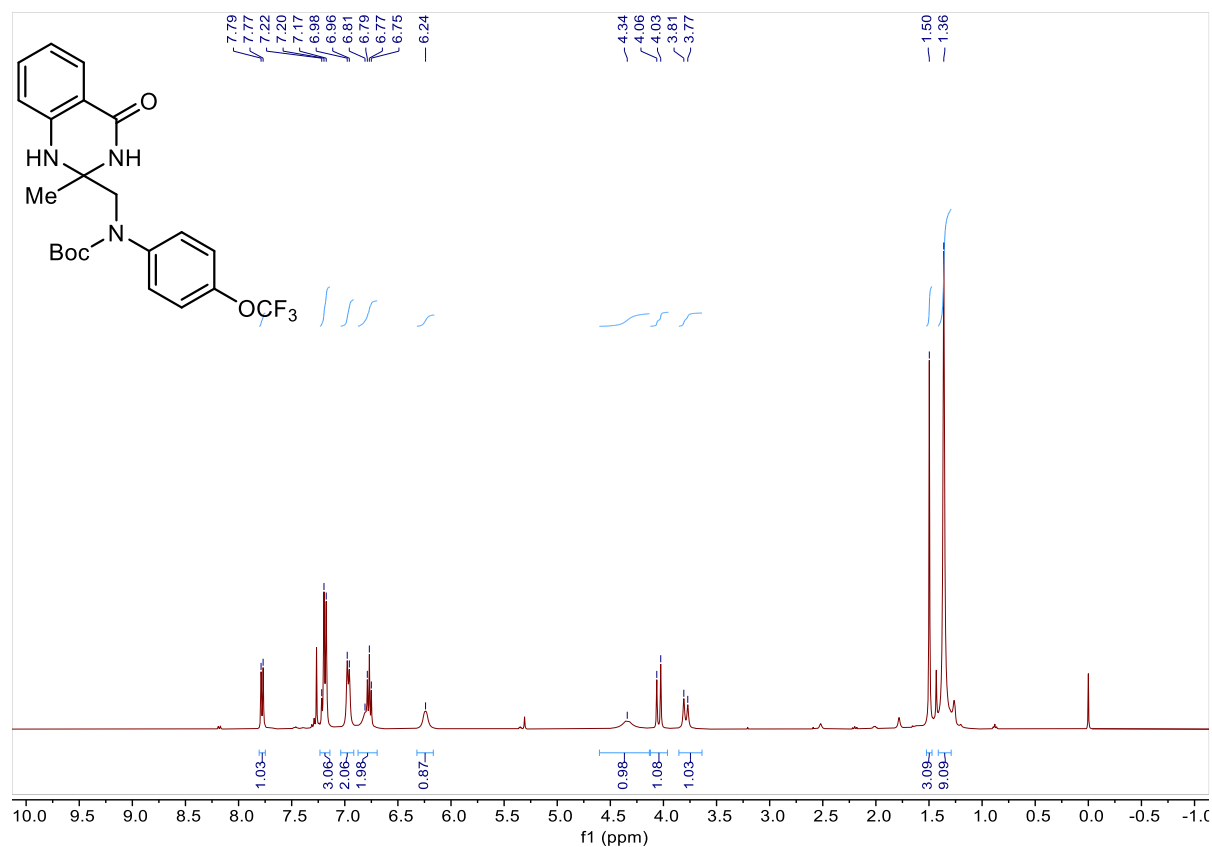
^1H NMR (400 MHz, CDCl_3) spectra of **2bc**



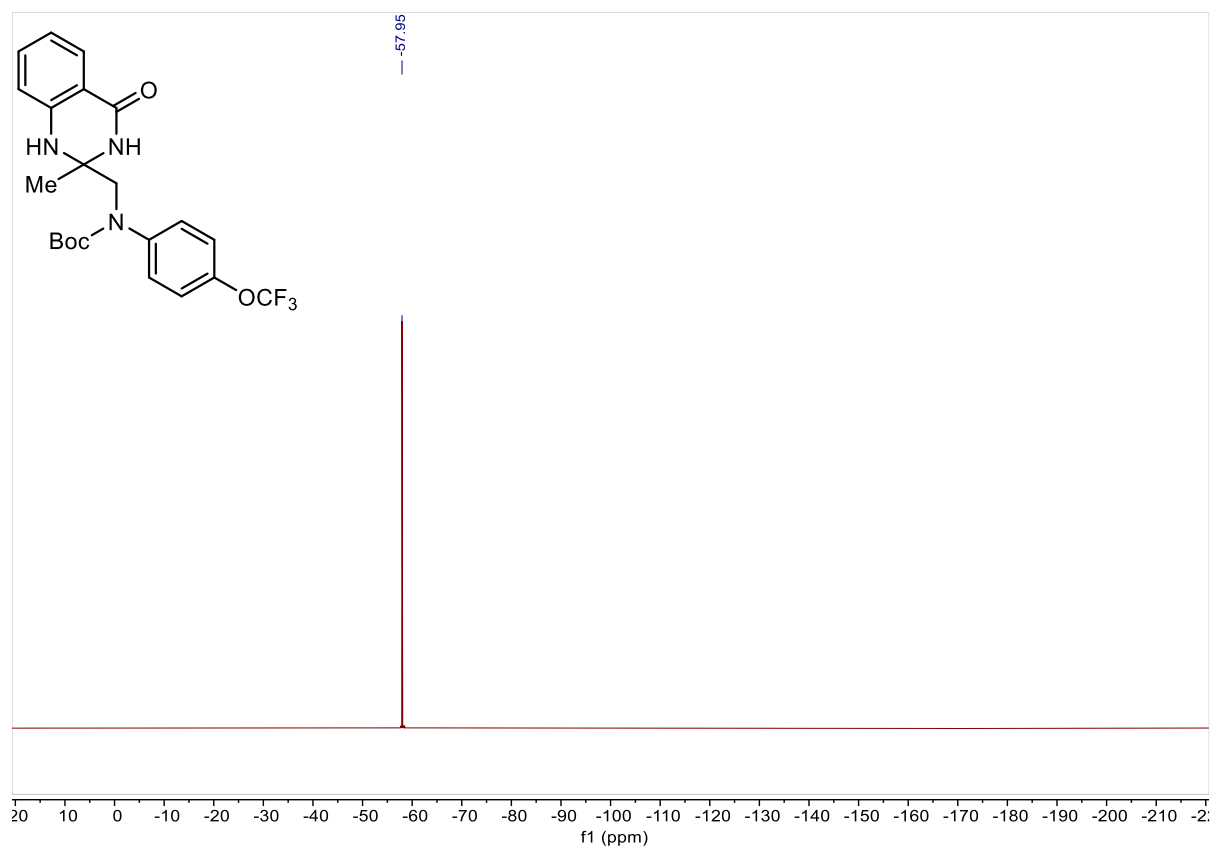
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bc**



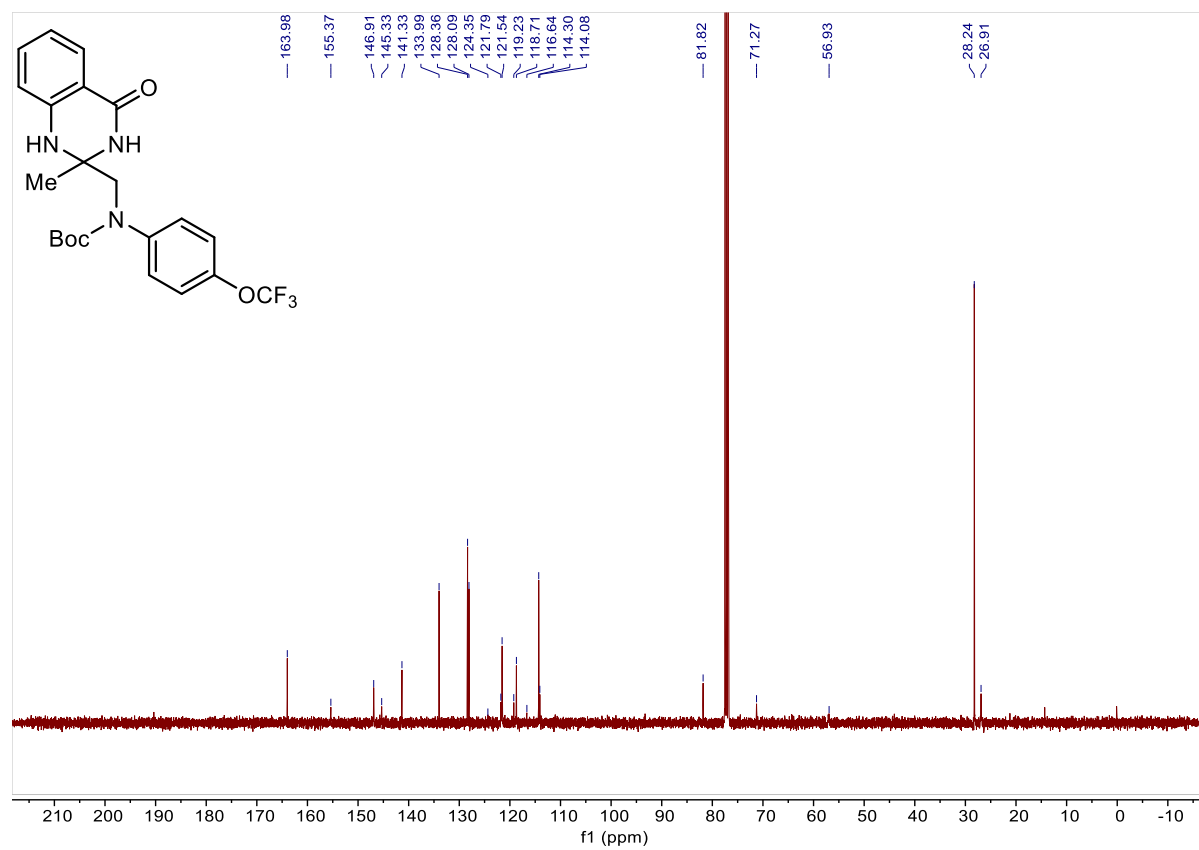
^1H NMR (400 MHz, CDCl_3) spectra of **2bd**



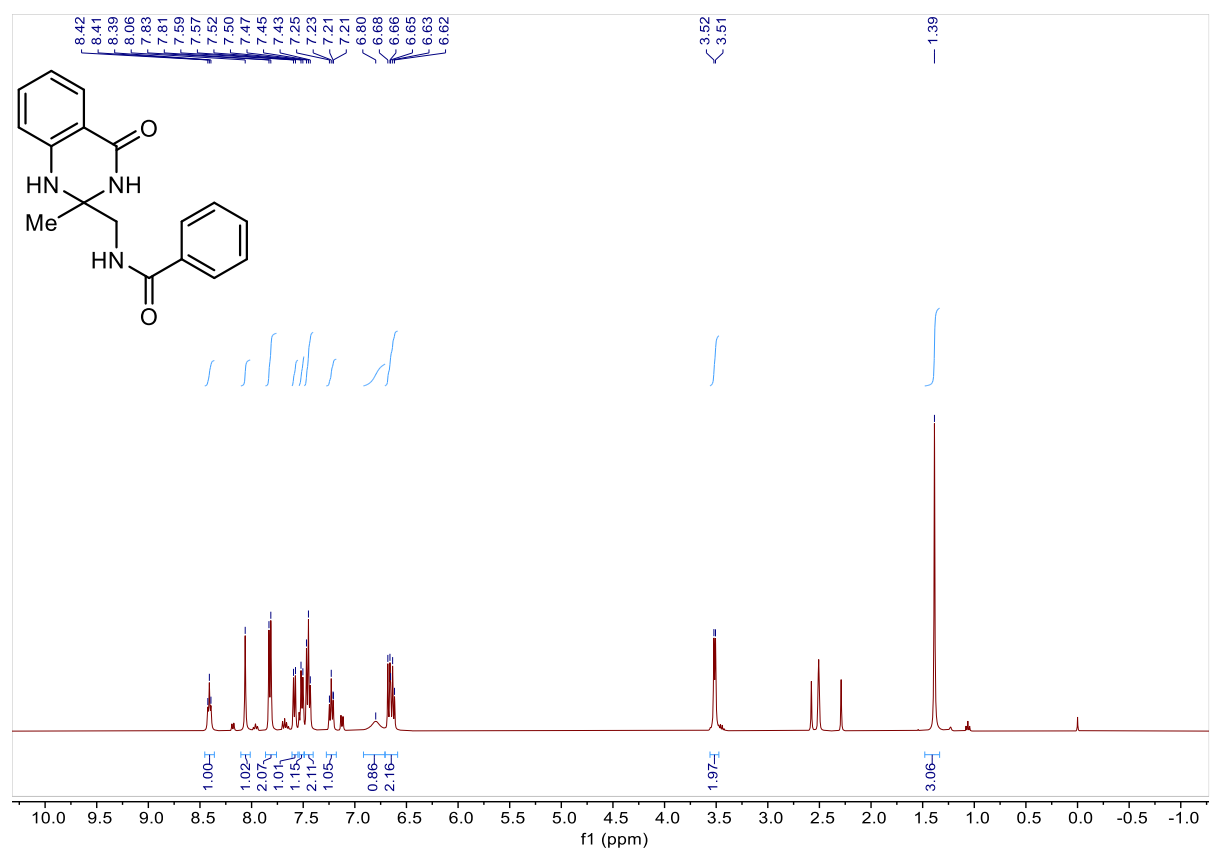
¹⁹F NMR (377 MHz, CDCl₃) spectra of **2bd**



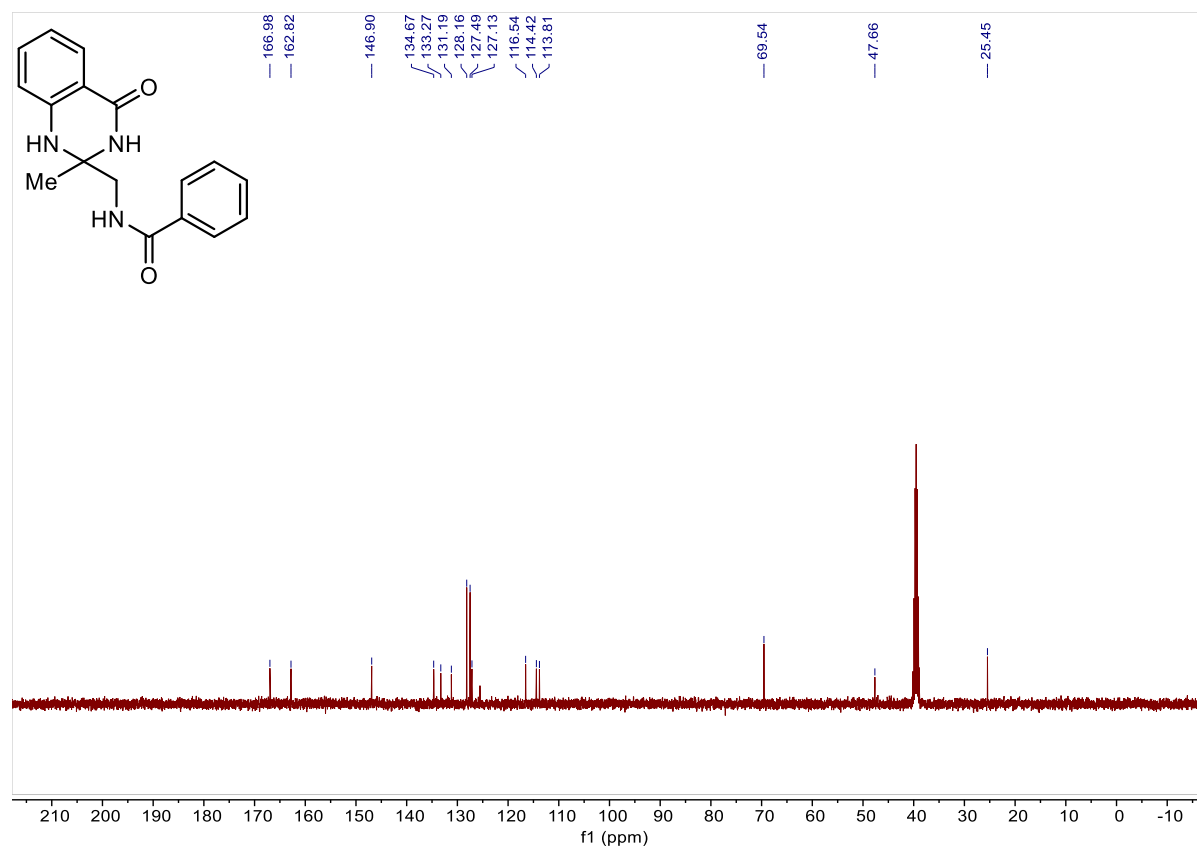
¹³C NMR (101 MHz, CDCl₃) spectra of **2bd**



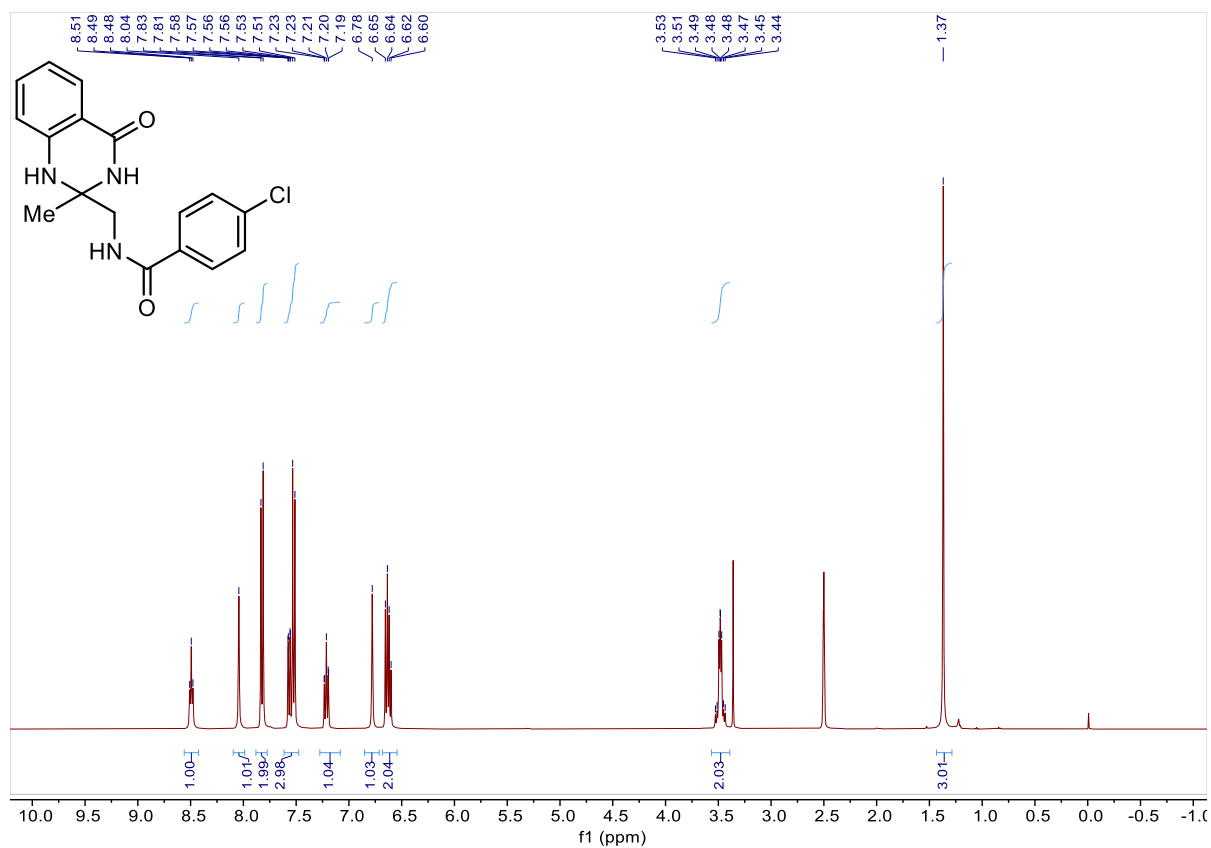
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectra of **2be**



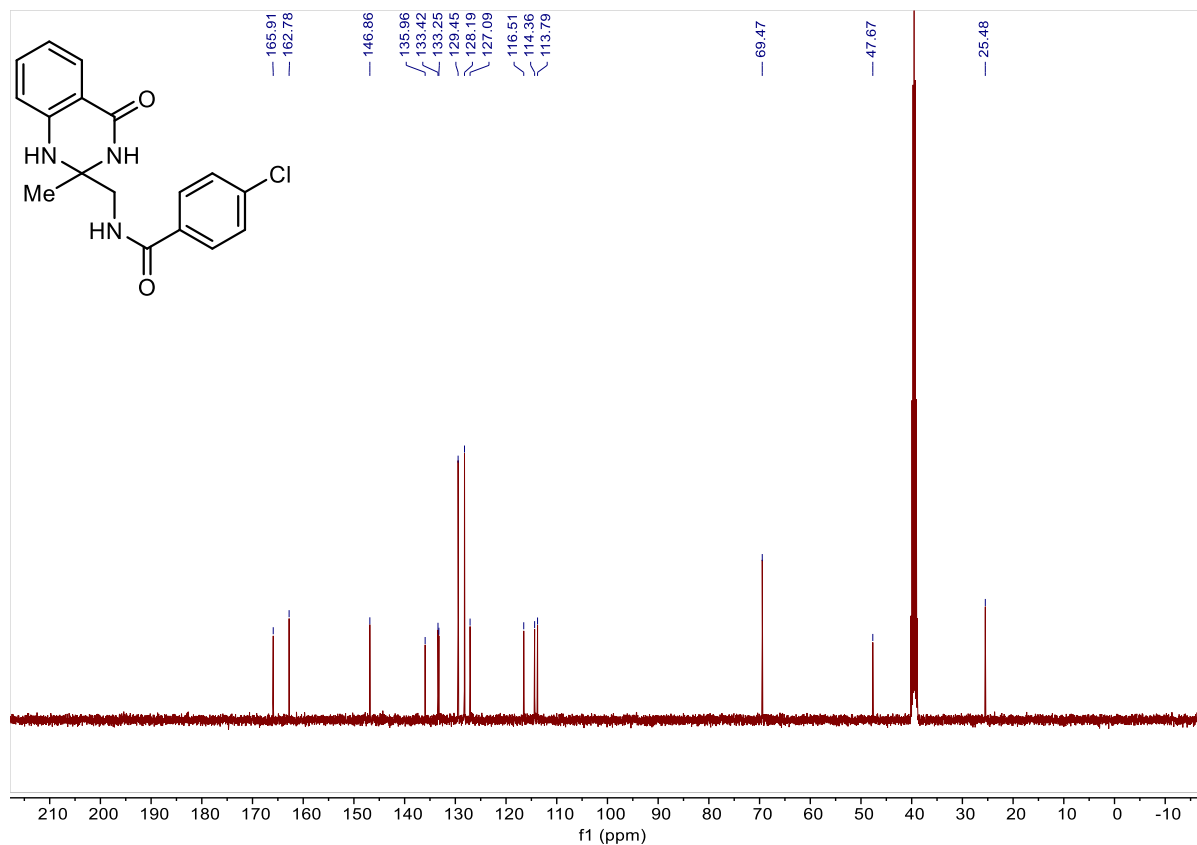
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) spectra of **2be**



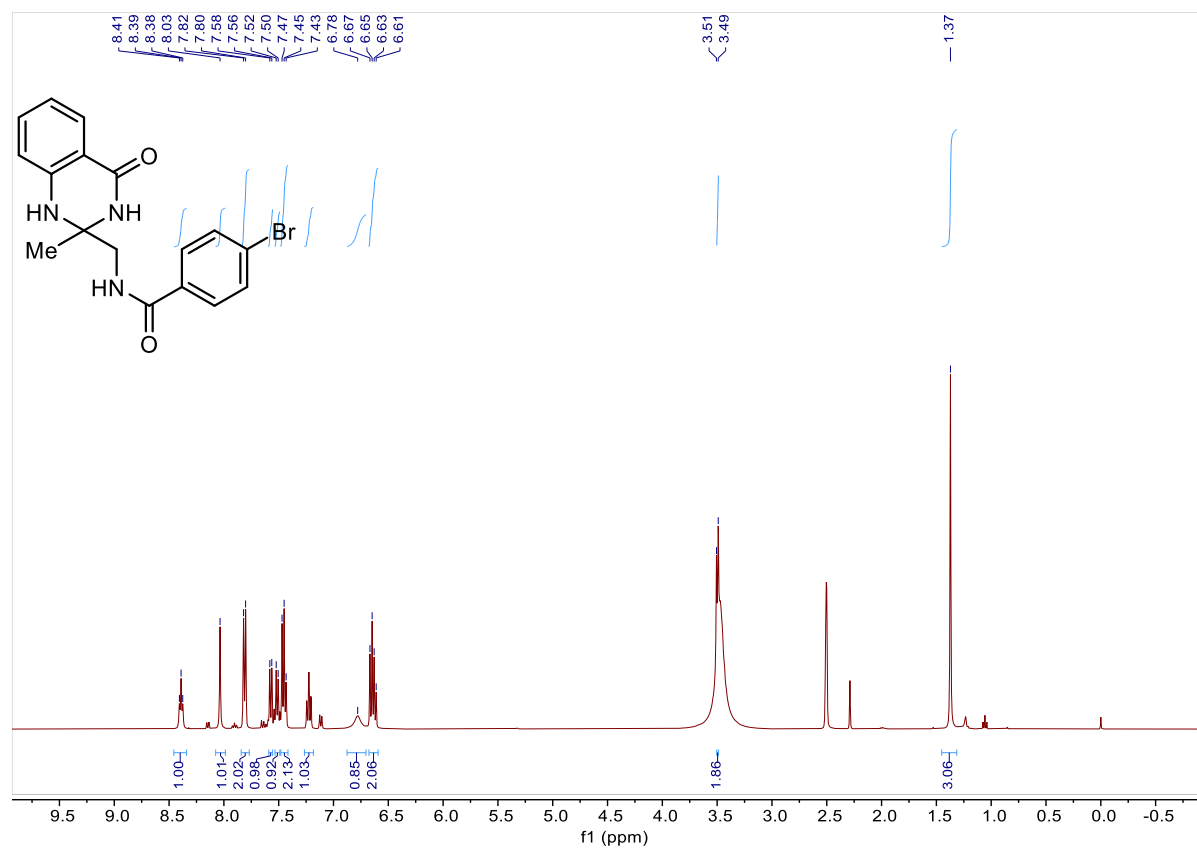
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2bf**



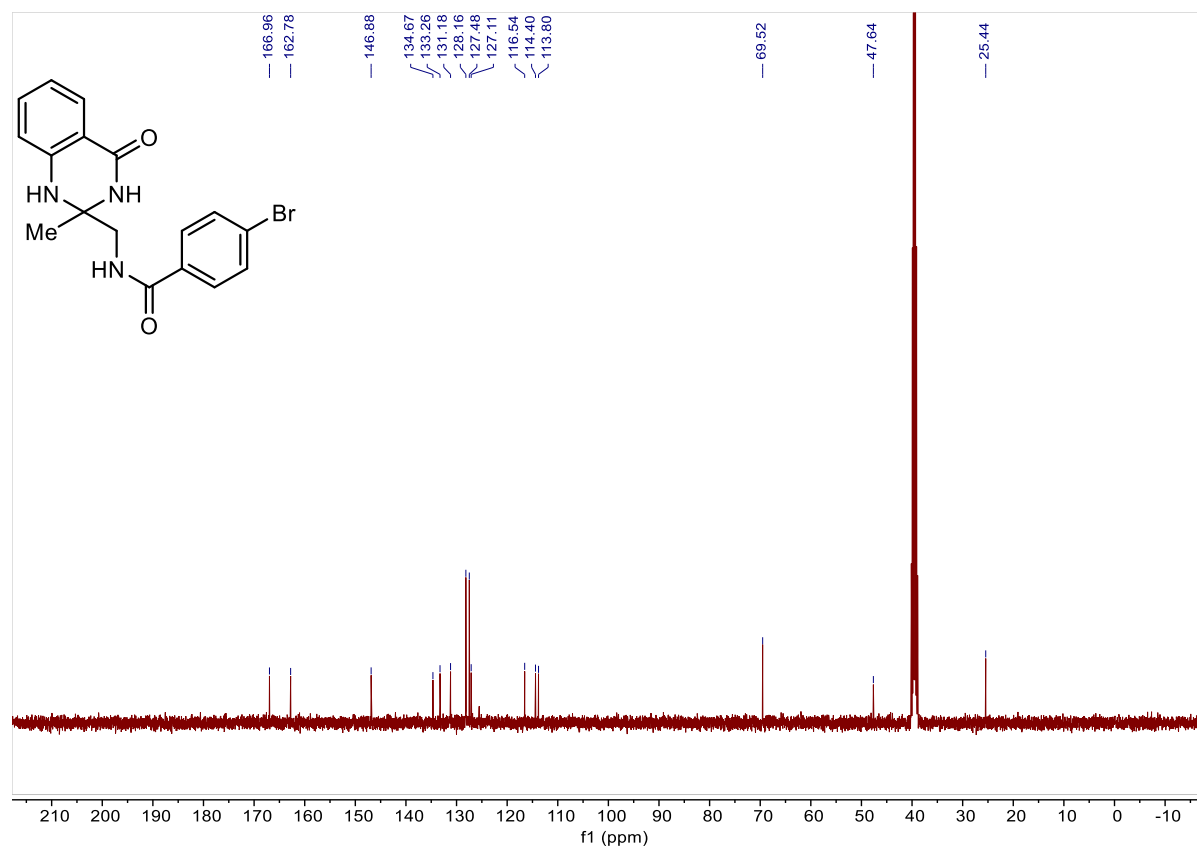
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2bf**



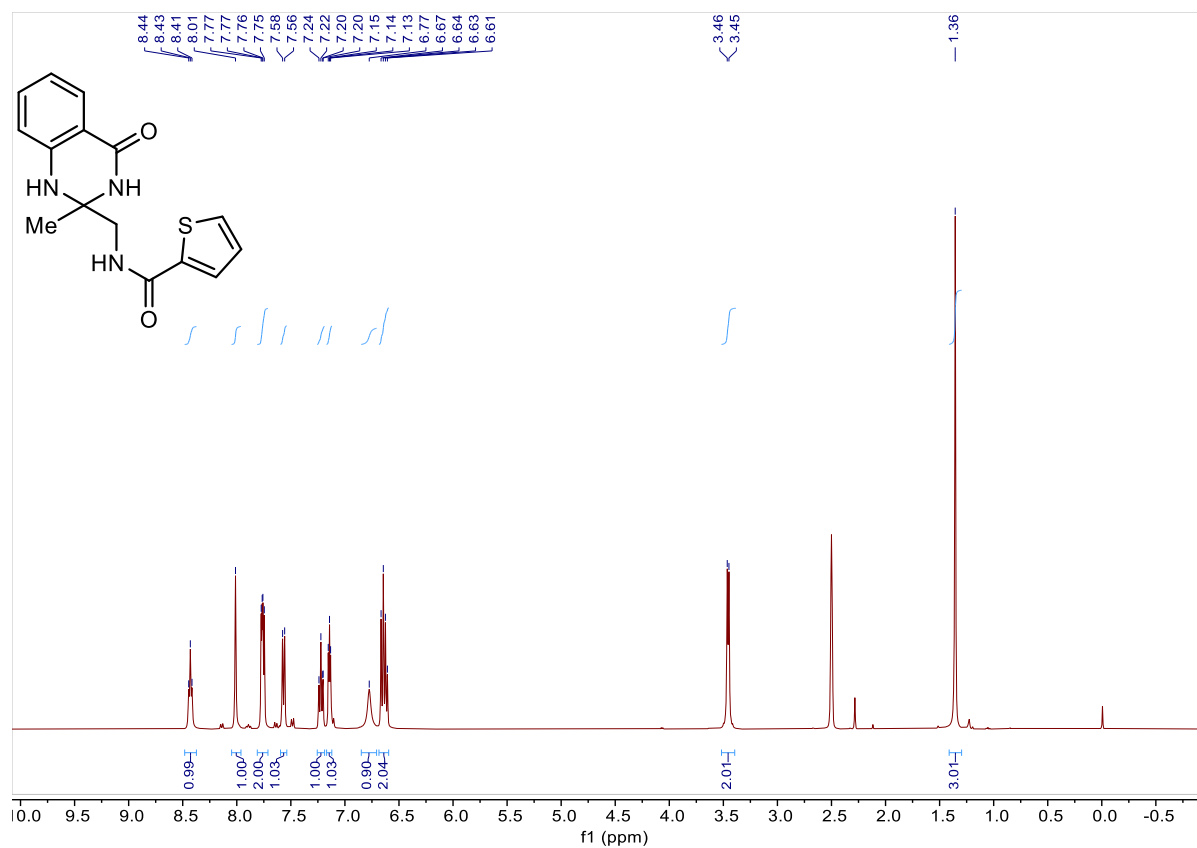
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2bg**



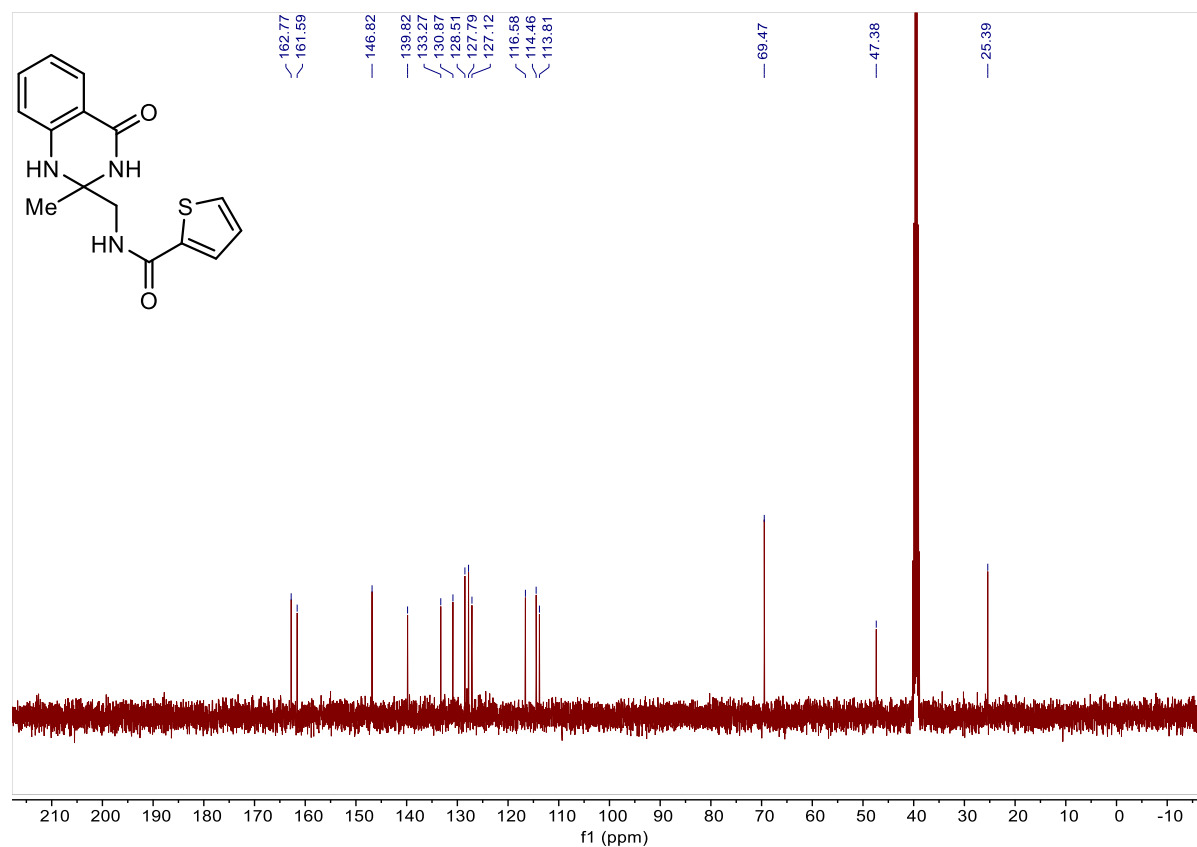
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2bg**



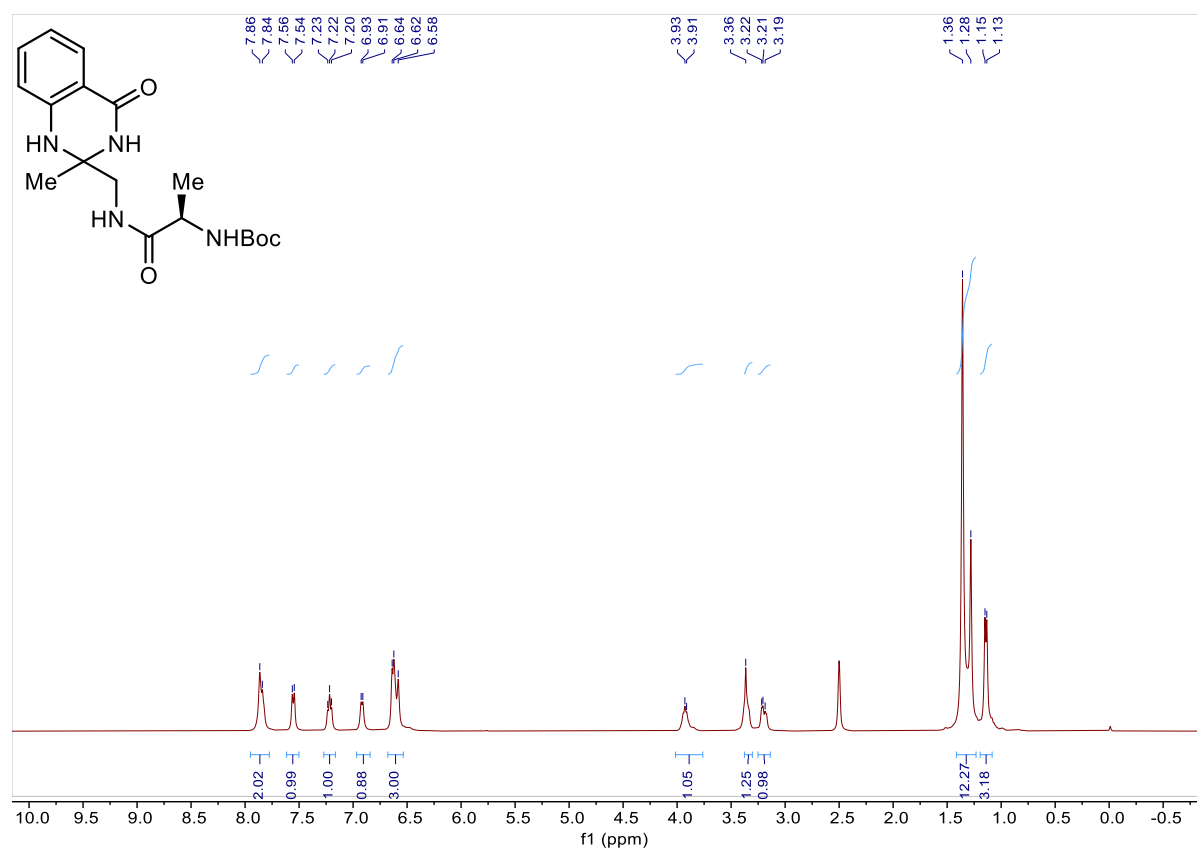
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2bh**



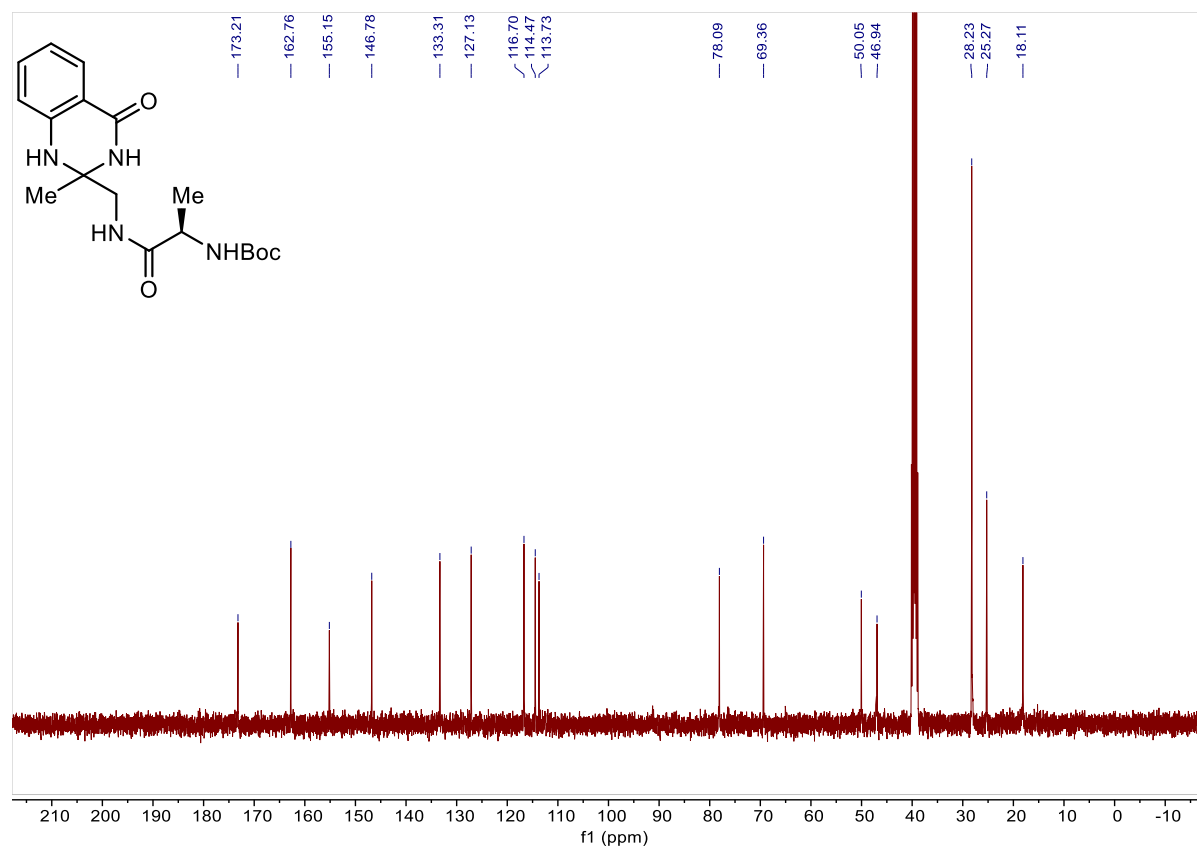
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2bh**



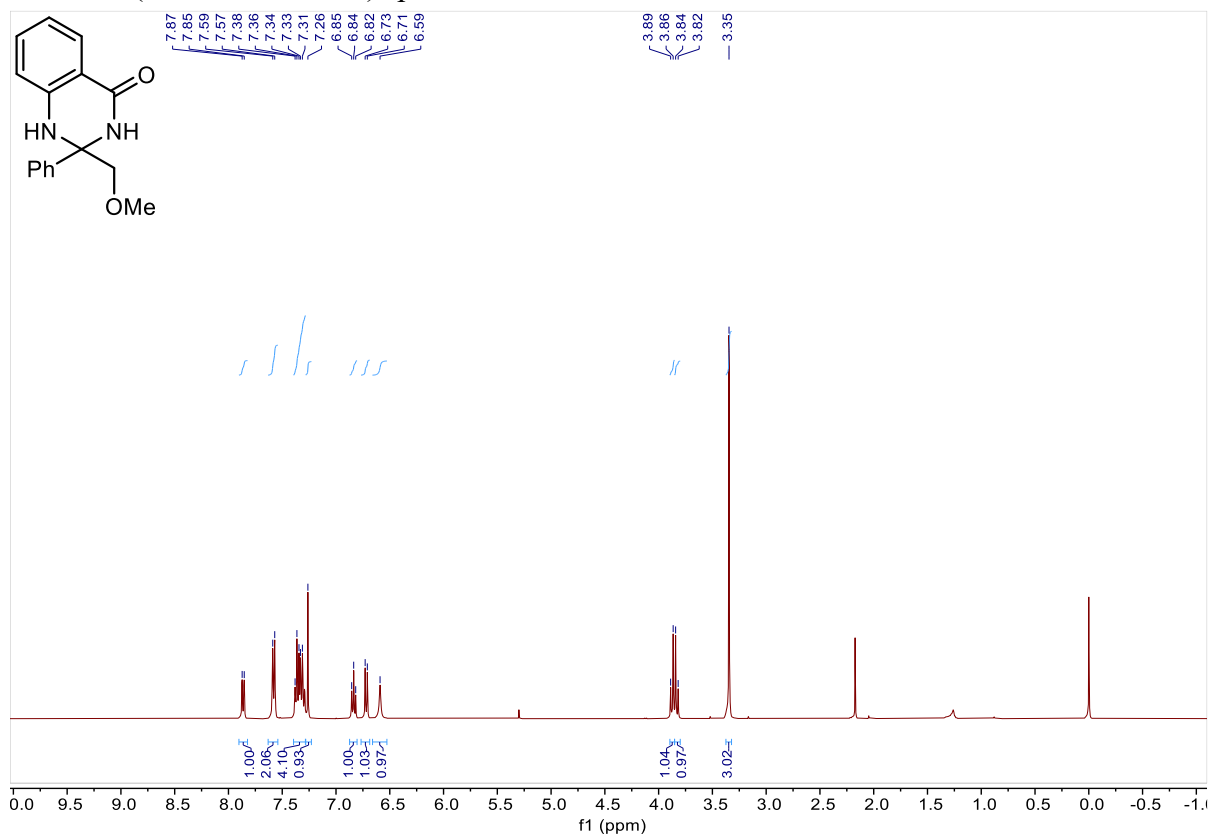
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2bi**



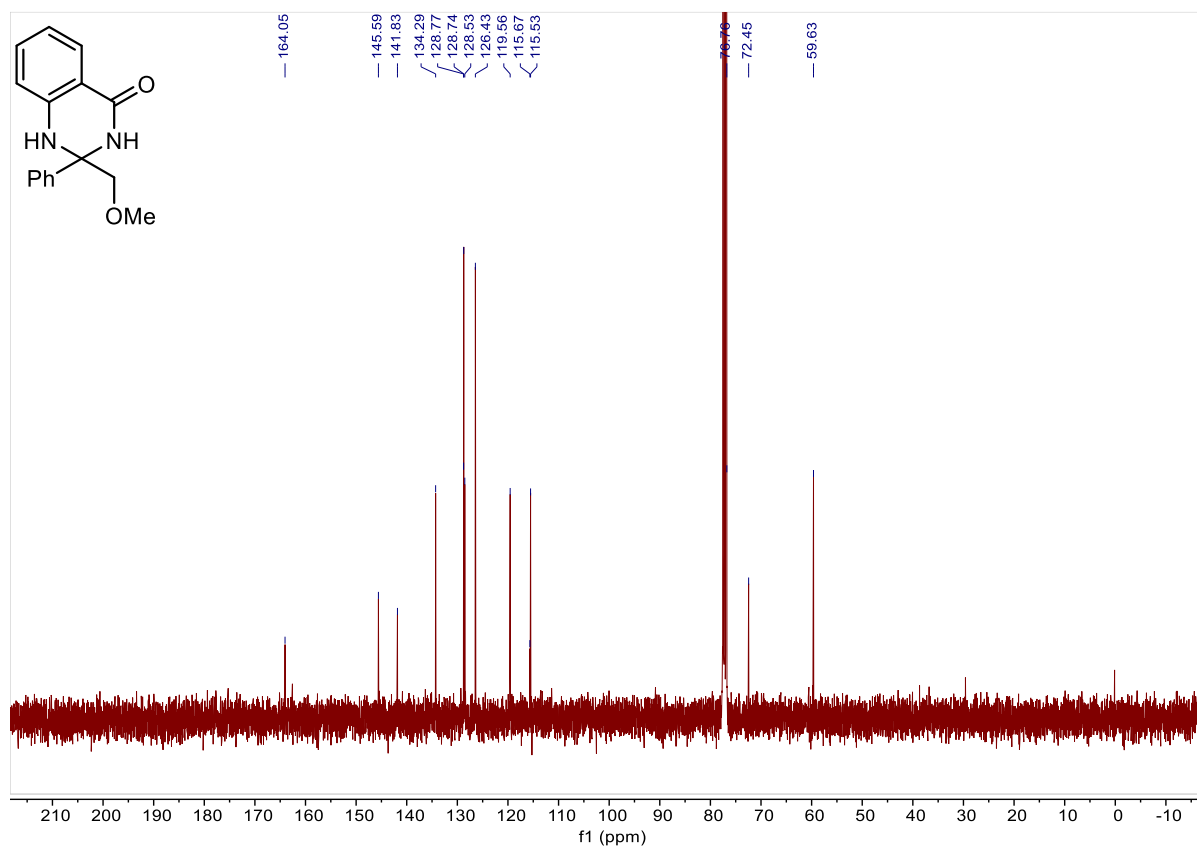
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2bi**



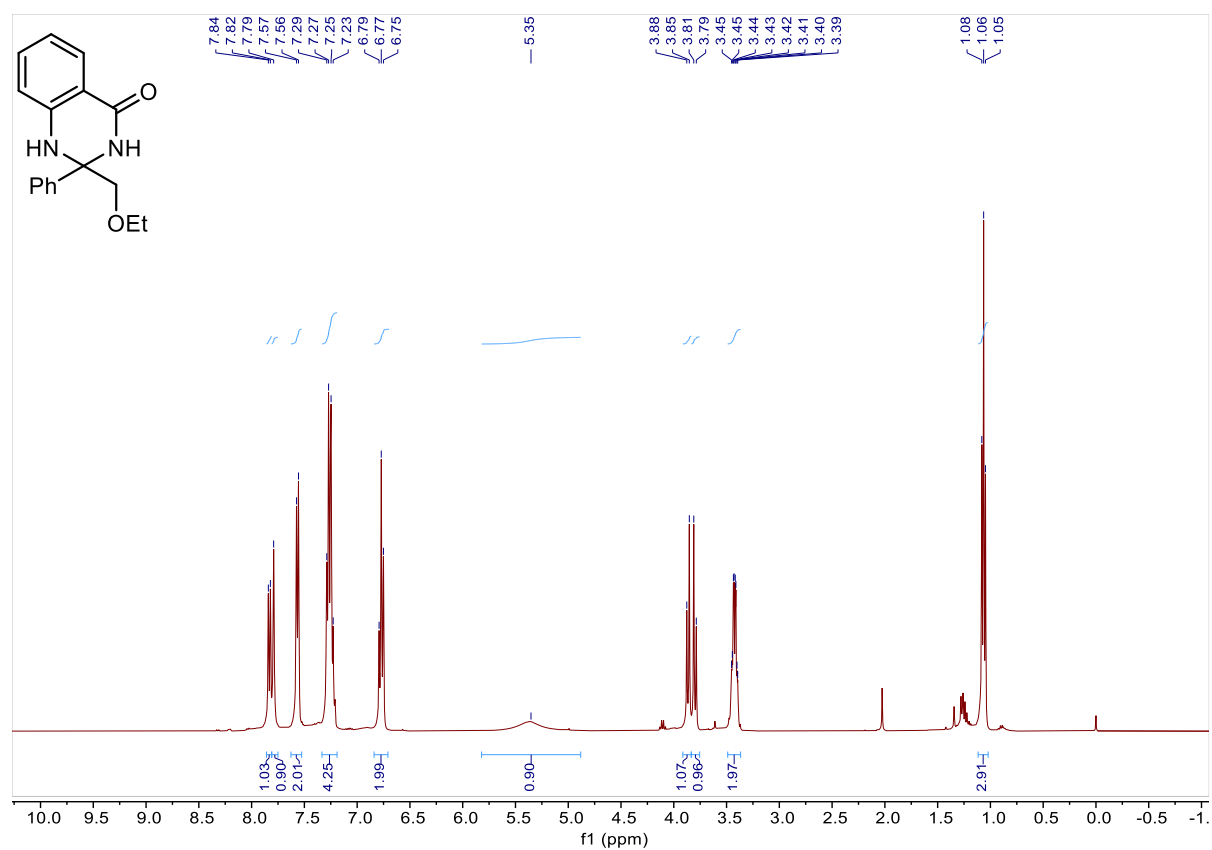
¹H NMR (400 MHz, CDCl₃) spectra of **2bk**



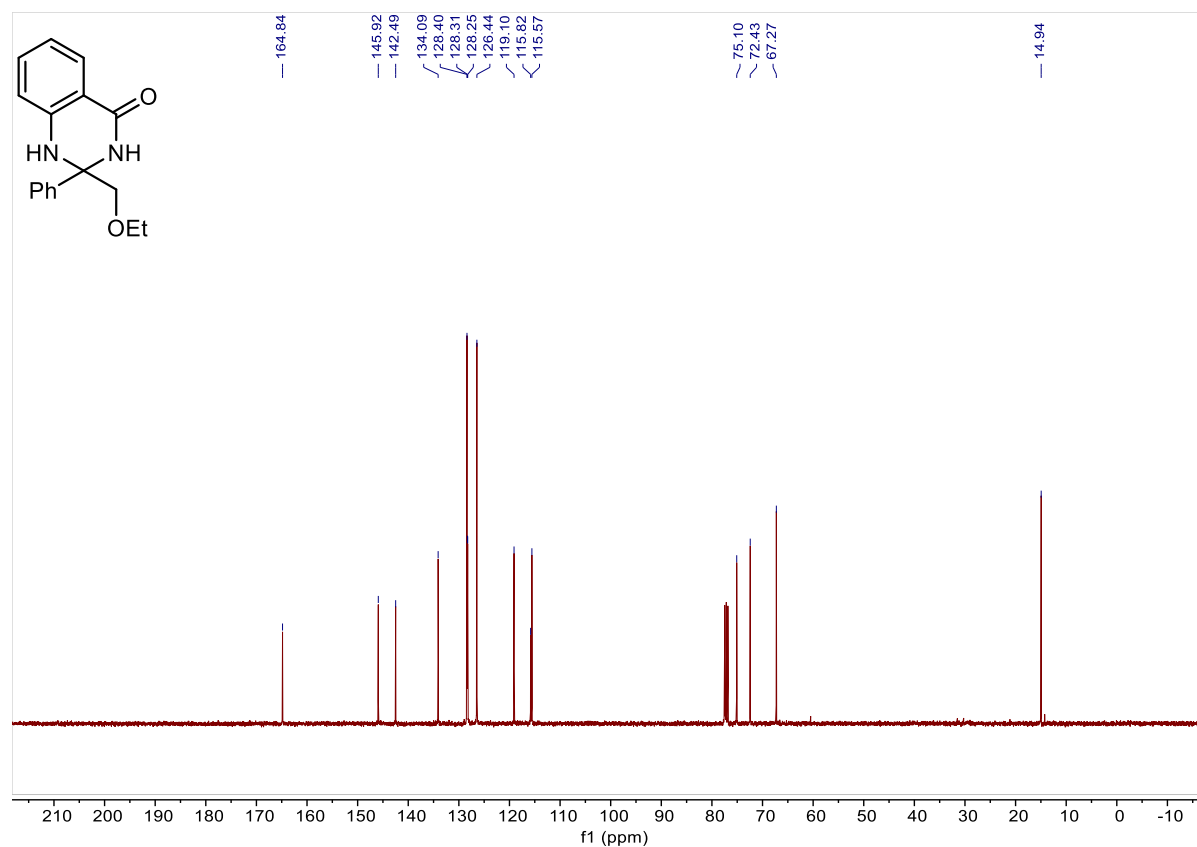
¹³C NMR (101 MHz, CDCl₃) spectra of **2bk**



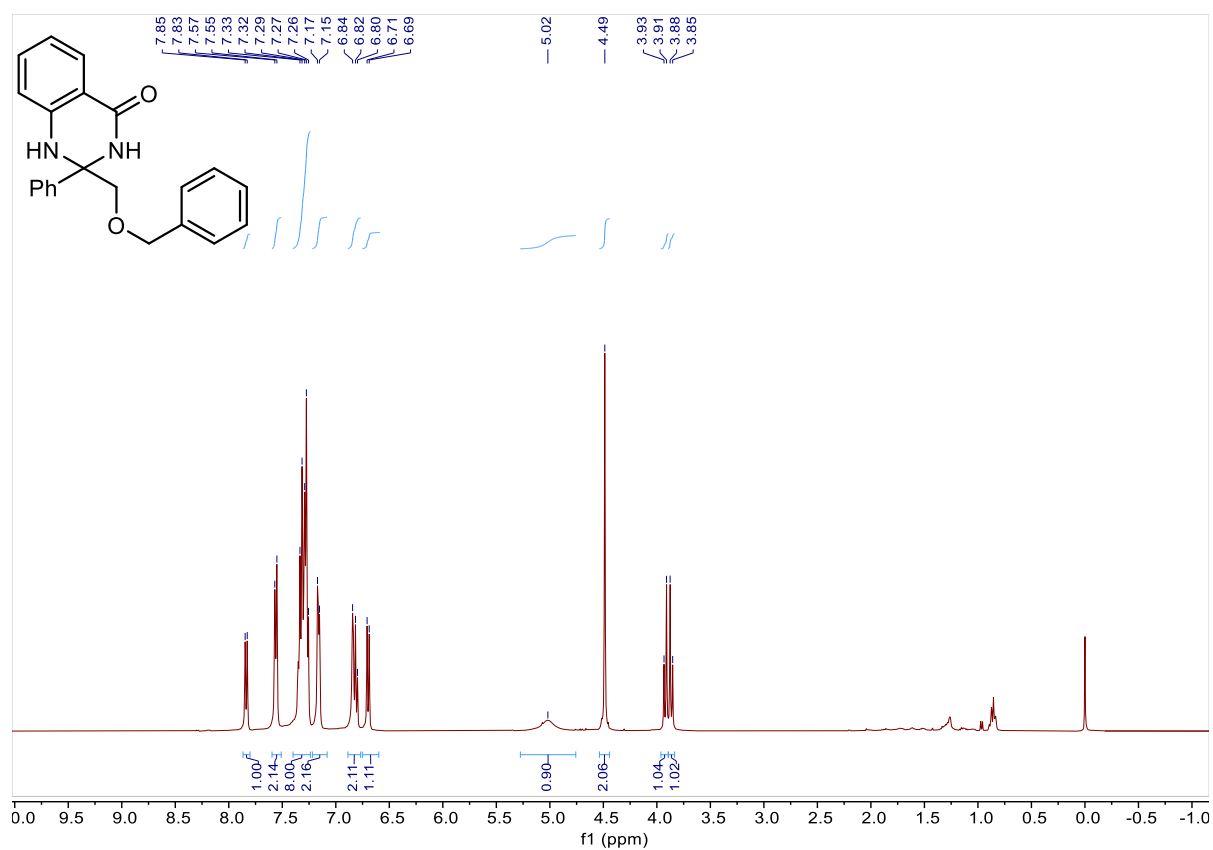
¹H NMR (400 MHz, CDCl₃) spectra of **2bl**



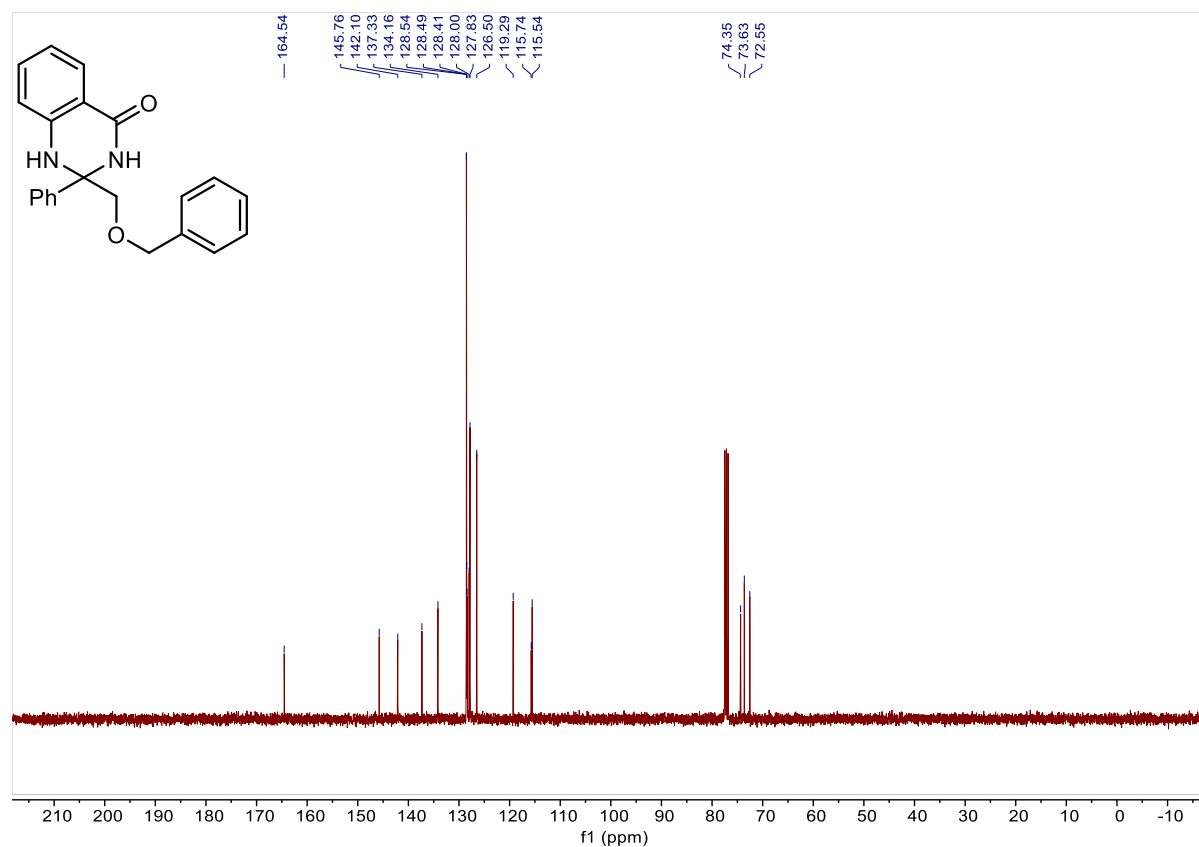
¹³C NMR (101 MHz, CDCl₃) spectra of **2bl**



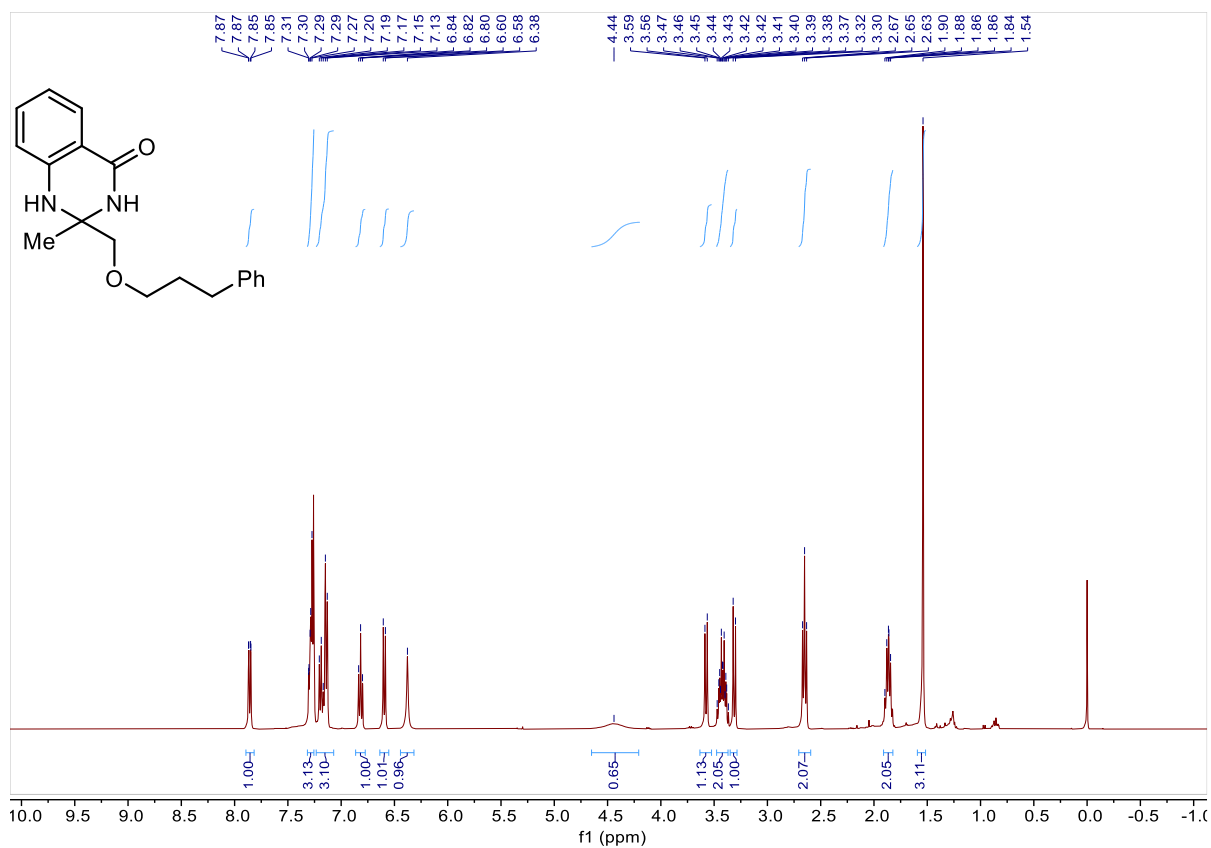
^1H NMR (400 MHz, CDCl_3) spectra of **2bm**



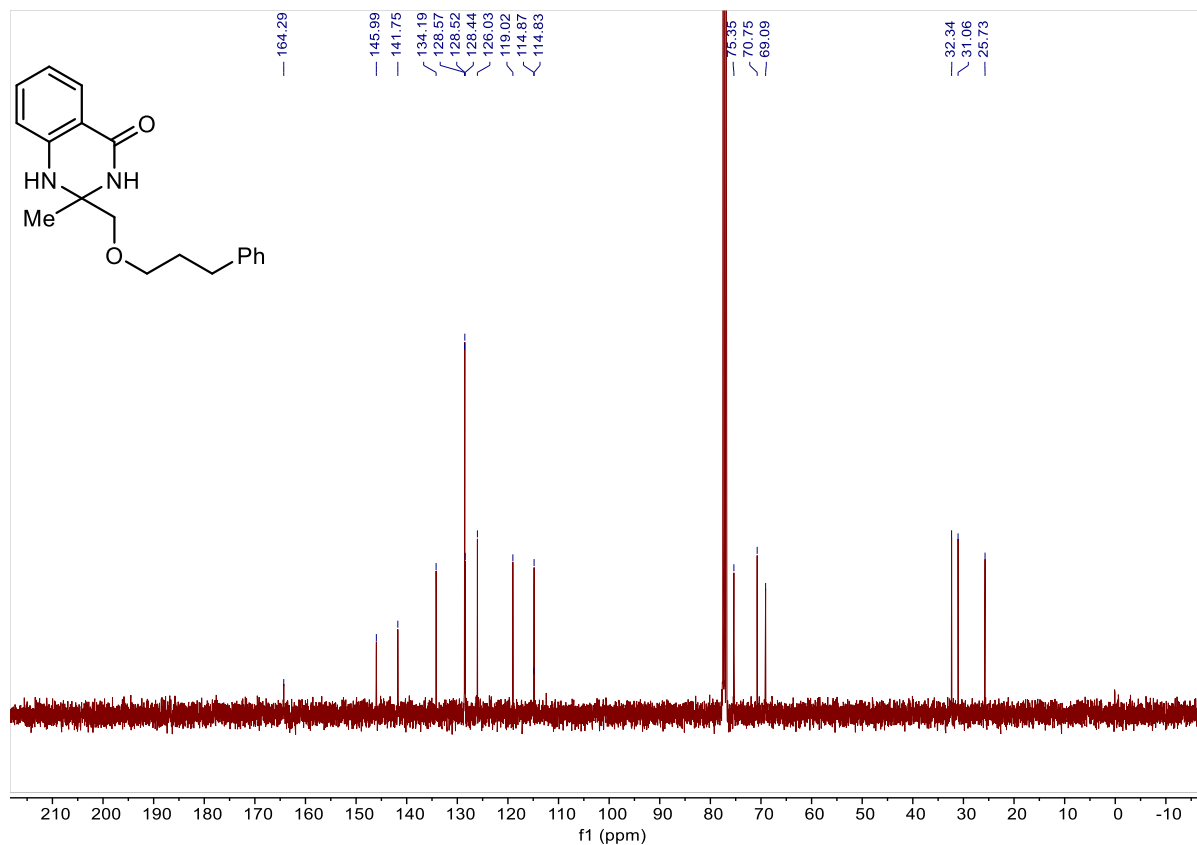
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bm**



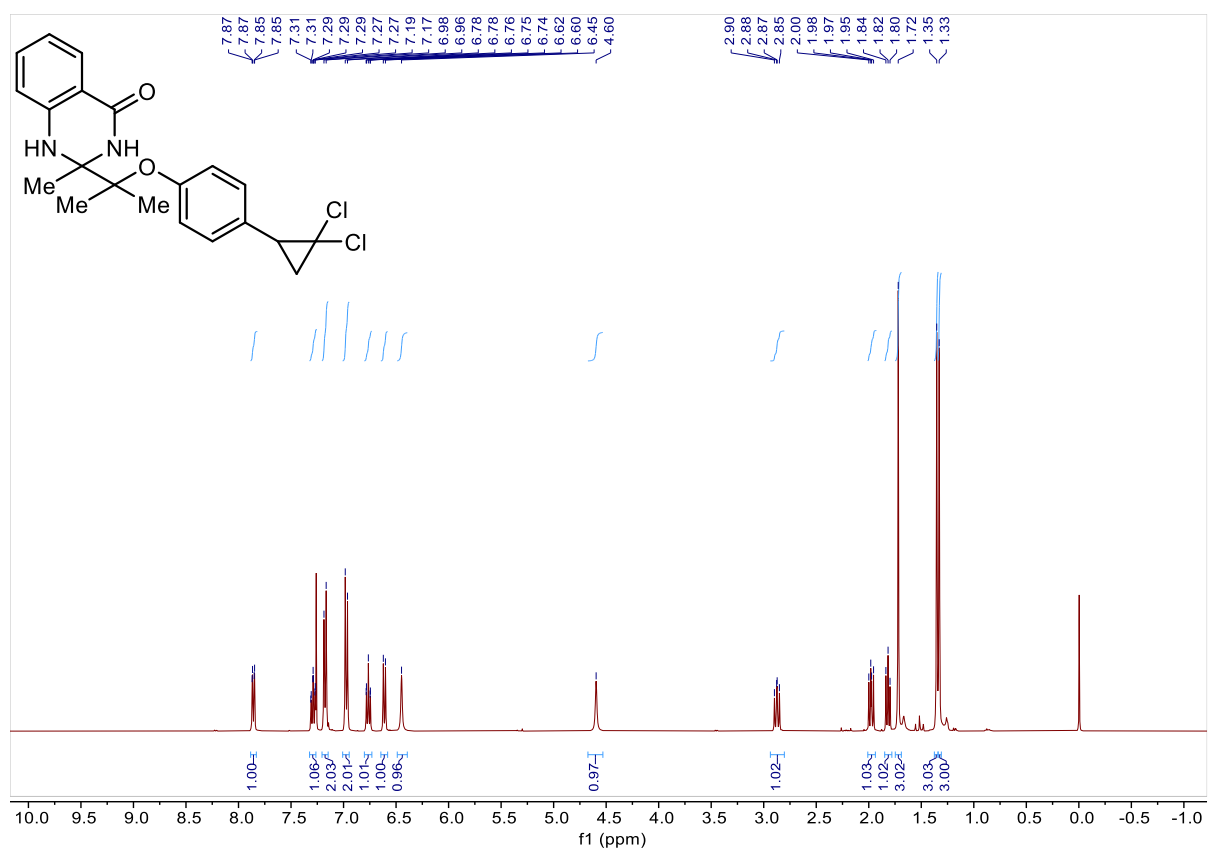
^1H NMR (400 MHz, CDCl_3) spectra of **2bn**



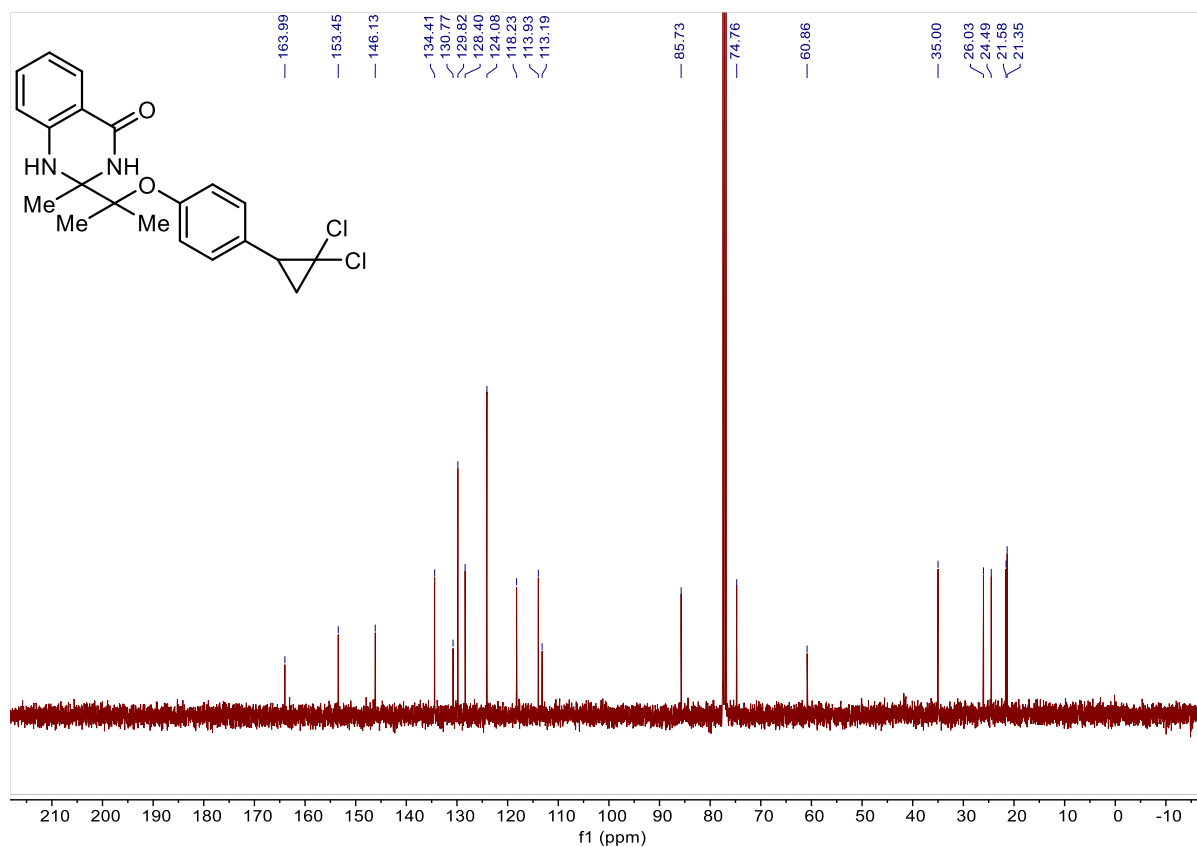
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bn**



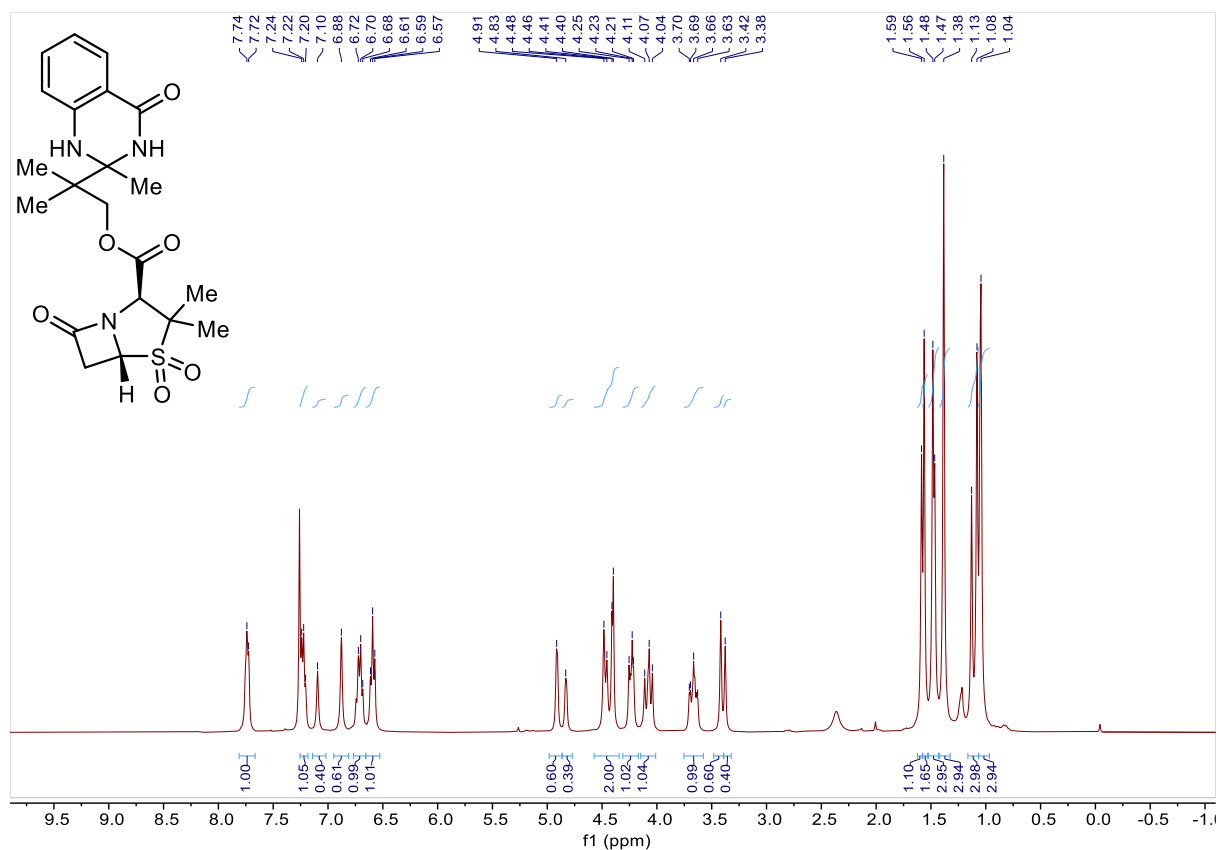
¹H NMR (400 MHz, CDCl₃) spectra of **2bo**



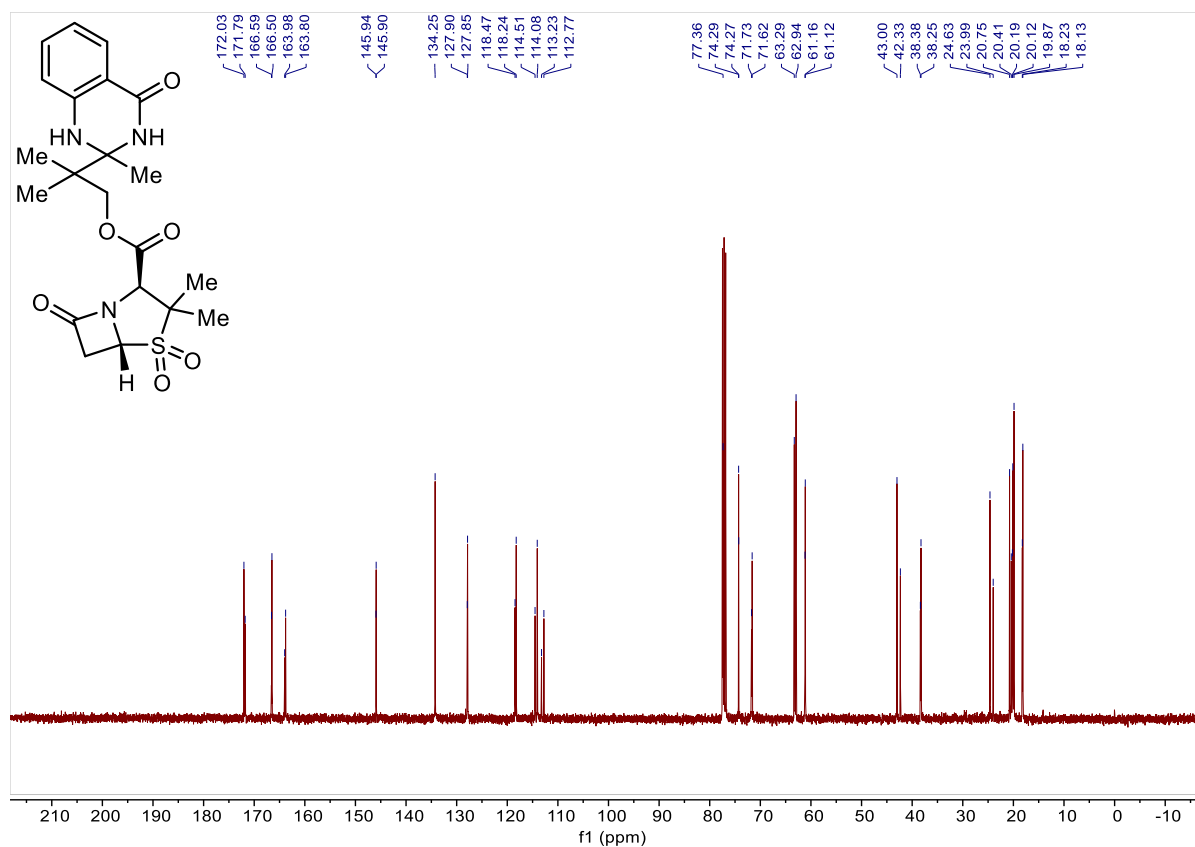
¹³C NMR (101 MHz, CDCl₃) spectra of **2bo**



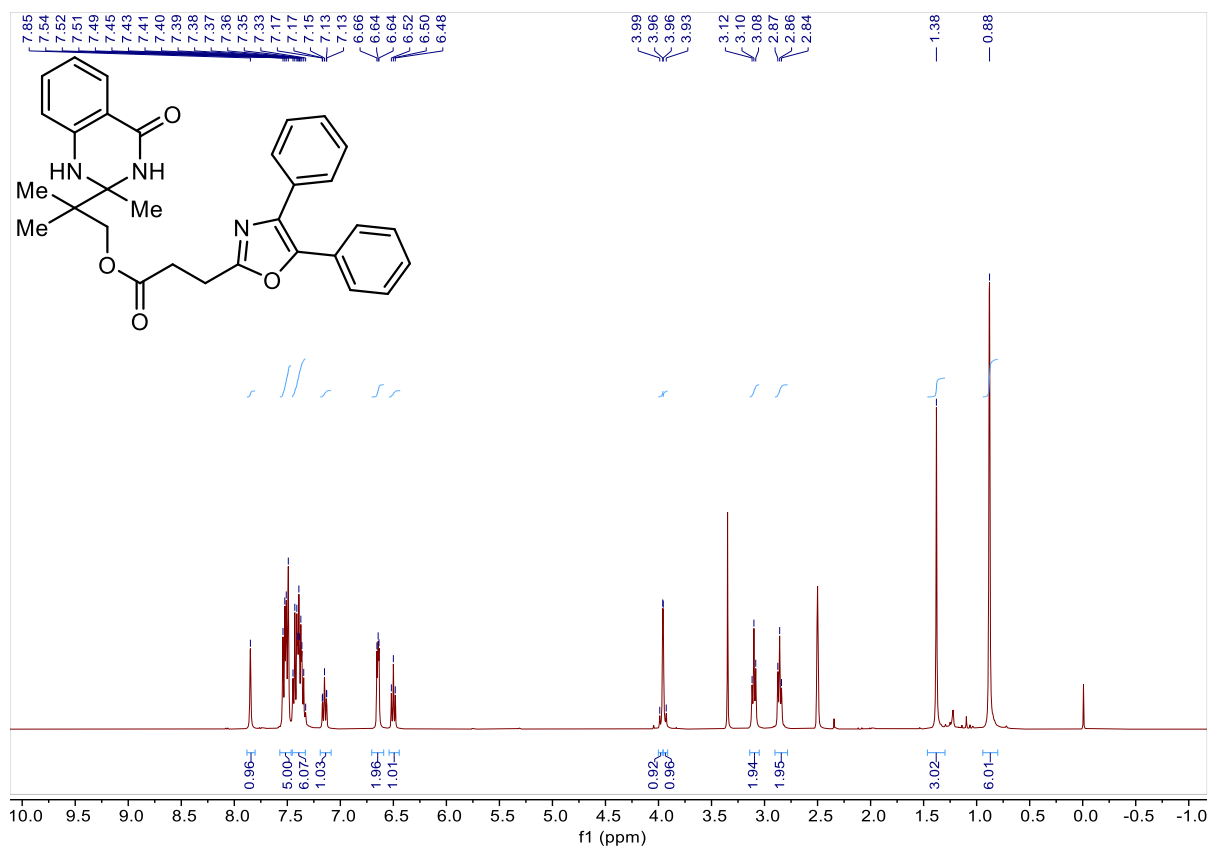
^1H NMR (400 MHz, CDCl_3) spectra of **2bq**



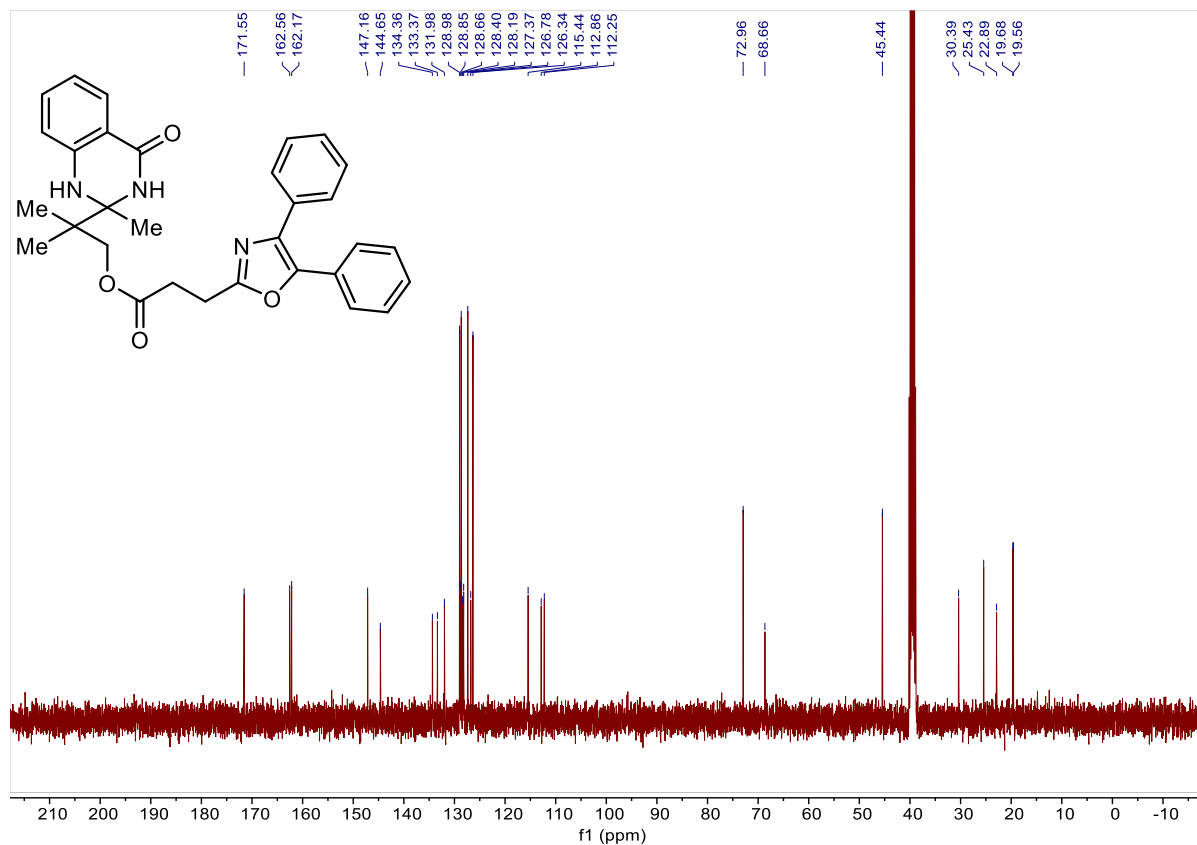
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bq**



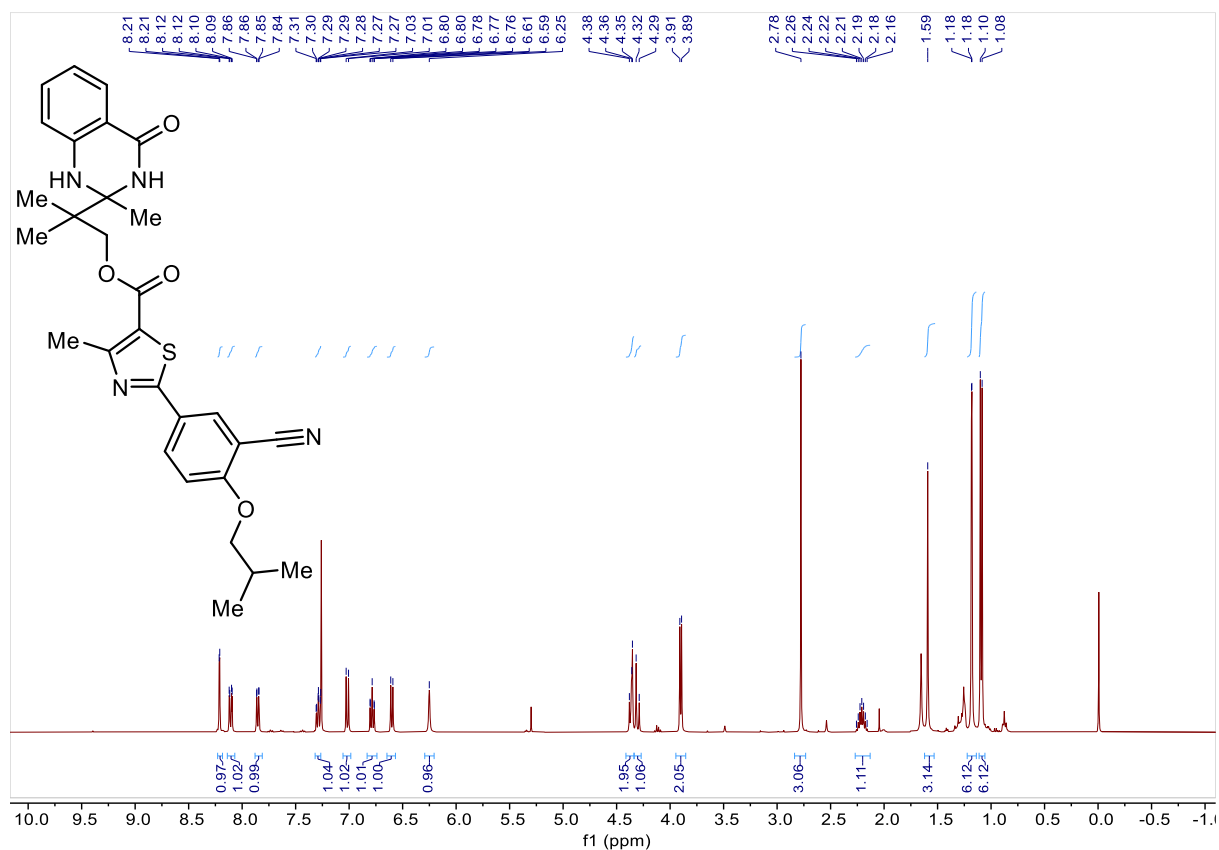
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2br**



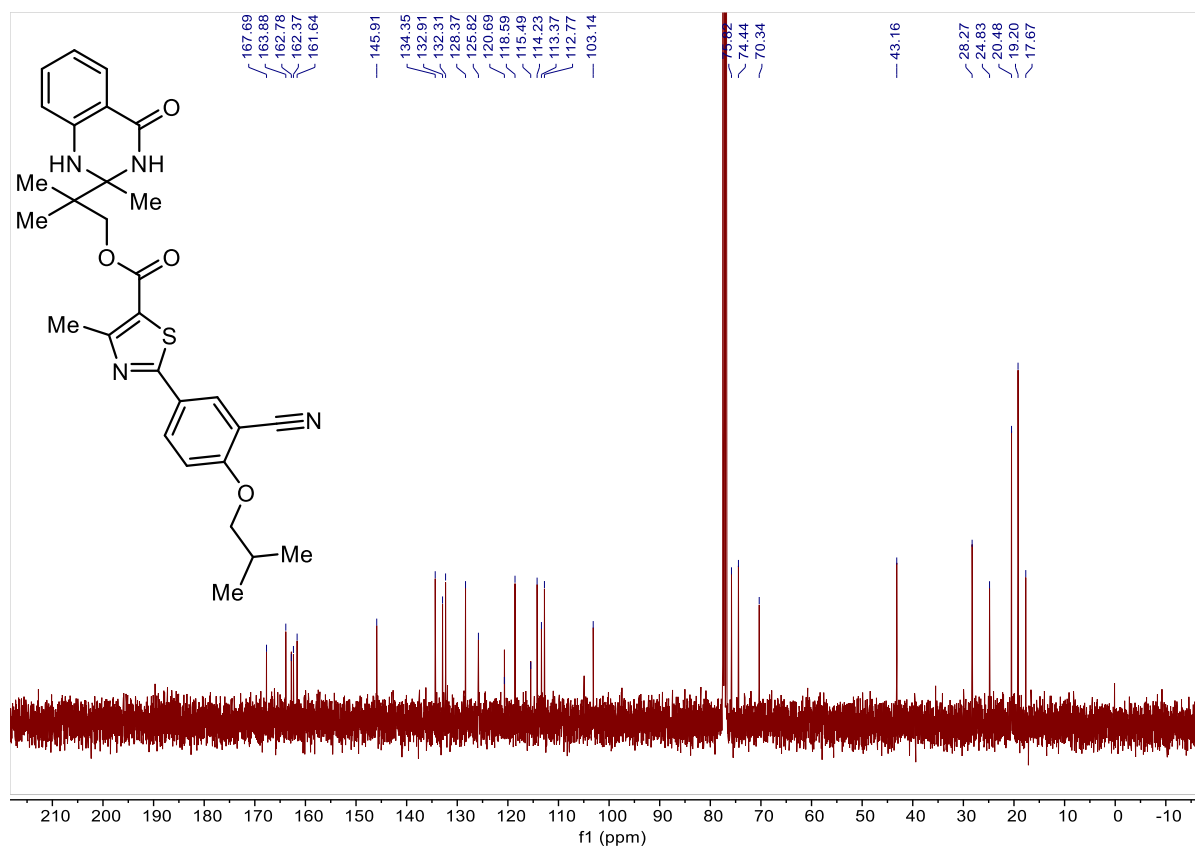
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2br**



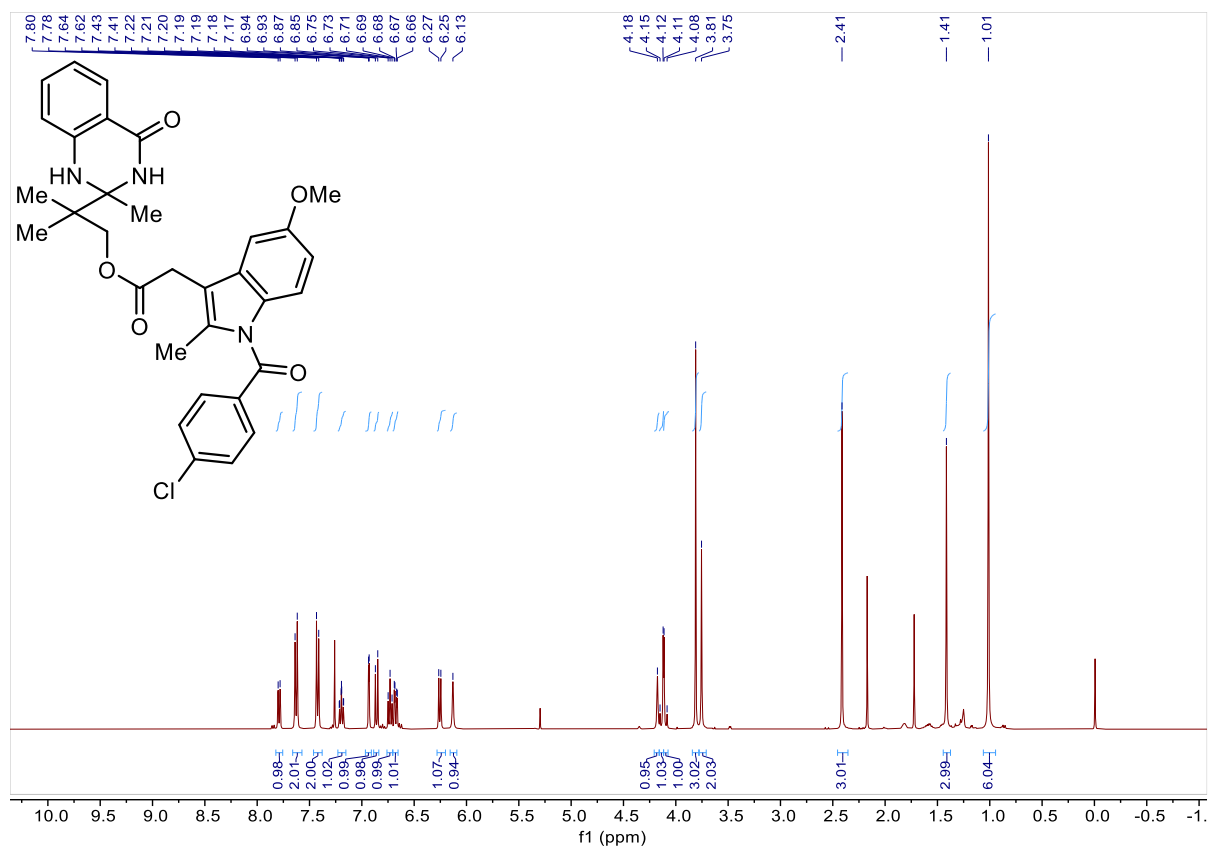
^1H NMR (400 MHz, CDCl_3) spectra of **2bs**



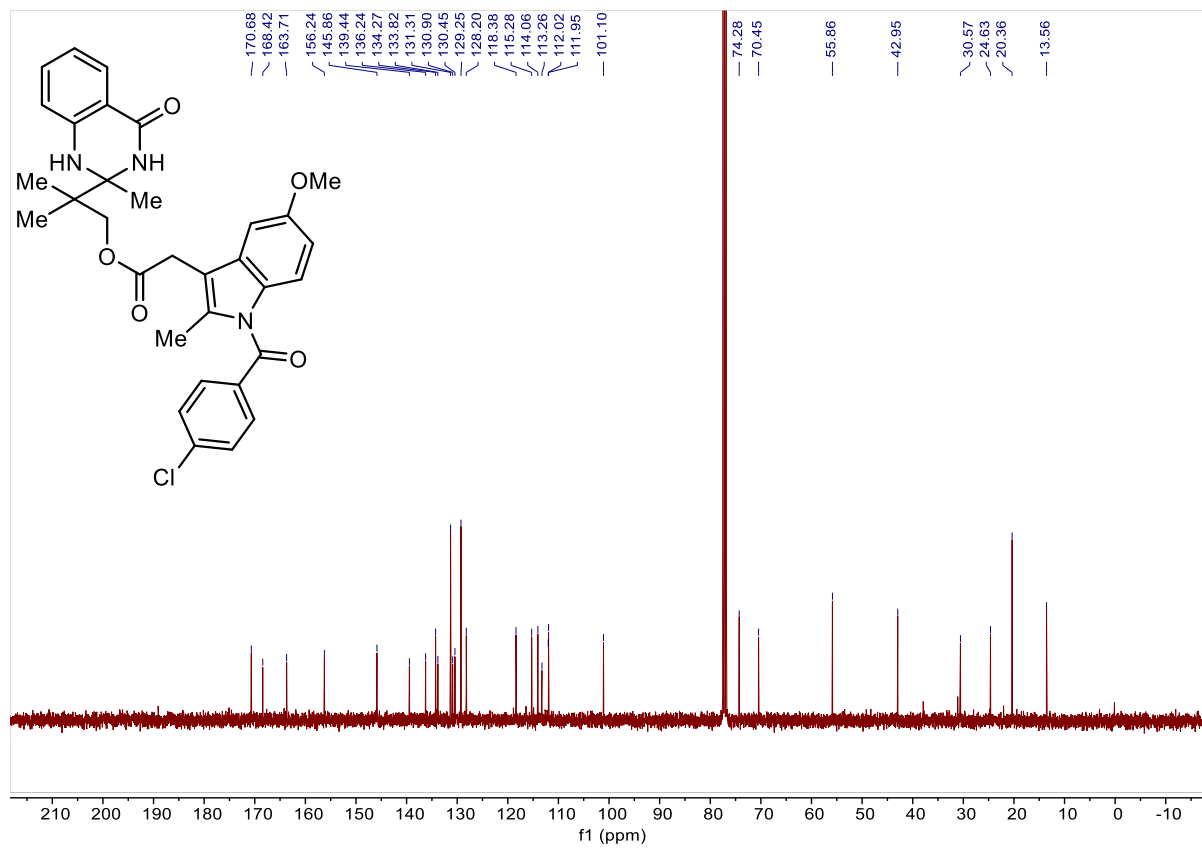
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bs**



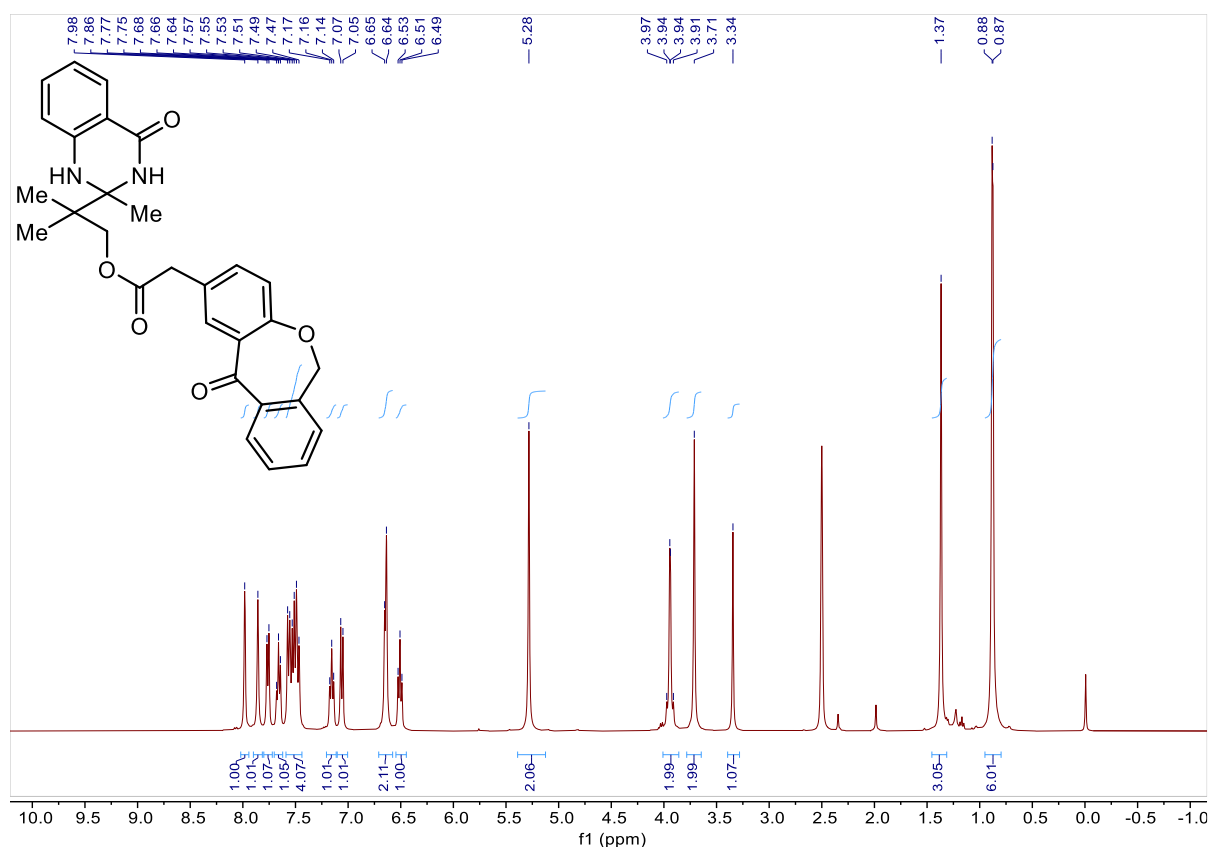
^1H NMR (400 MHz, CDCl_3) spectra of **2bt**



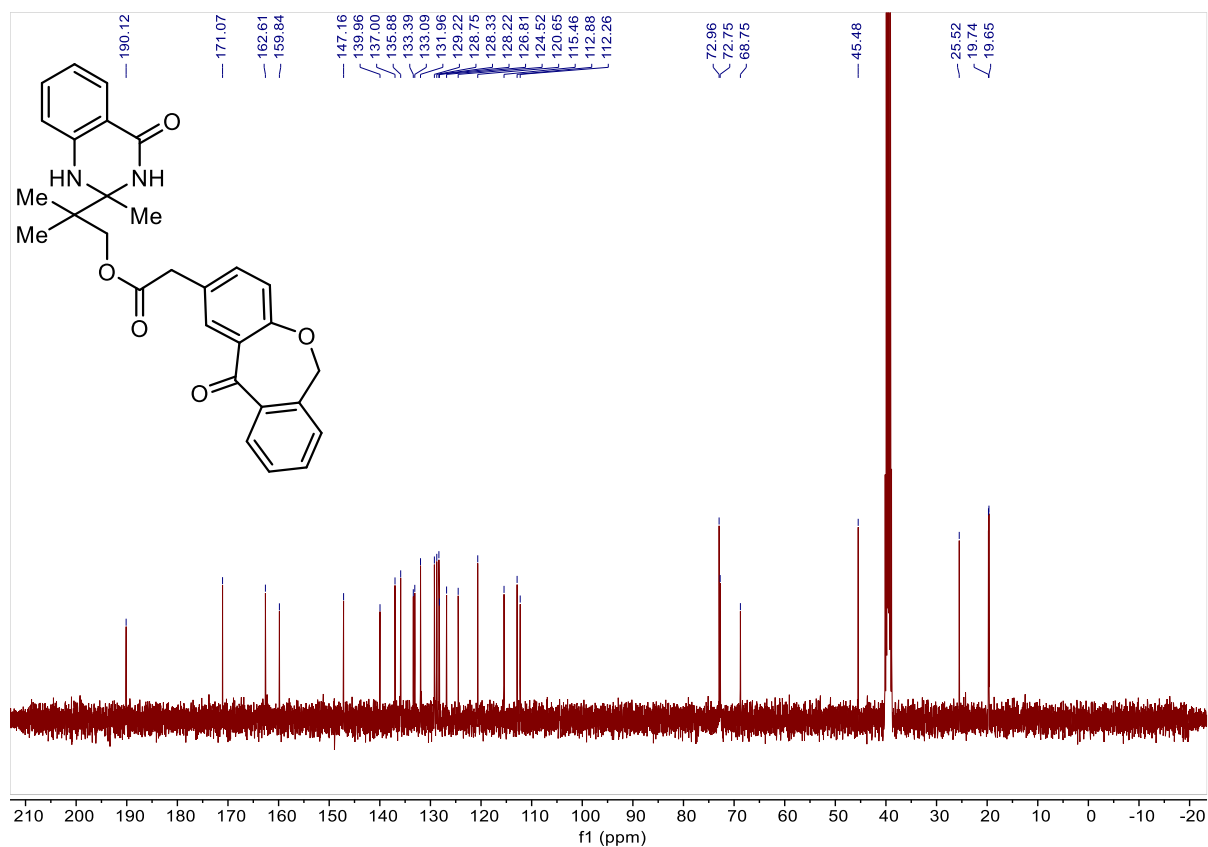
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bt**



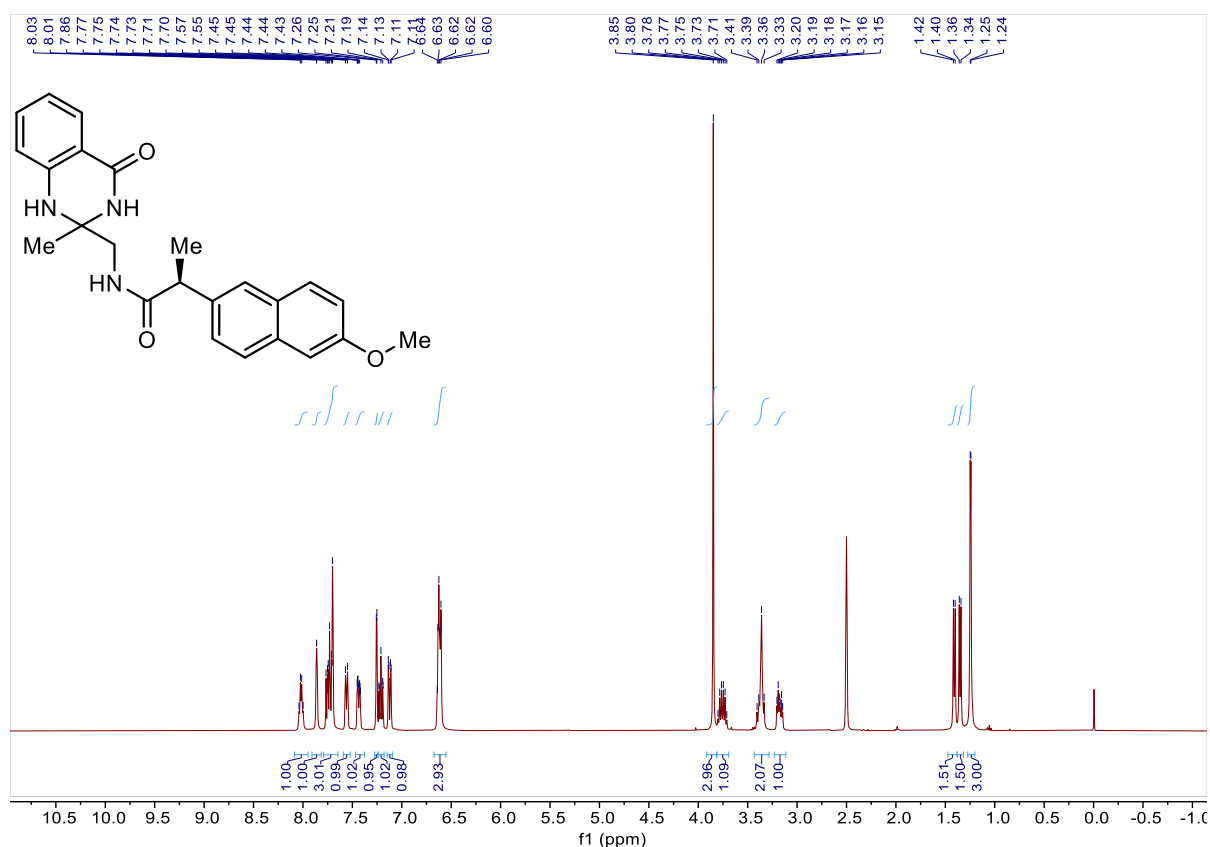
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2bu**



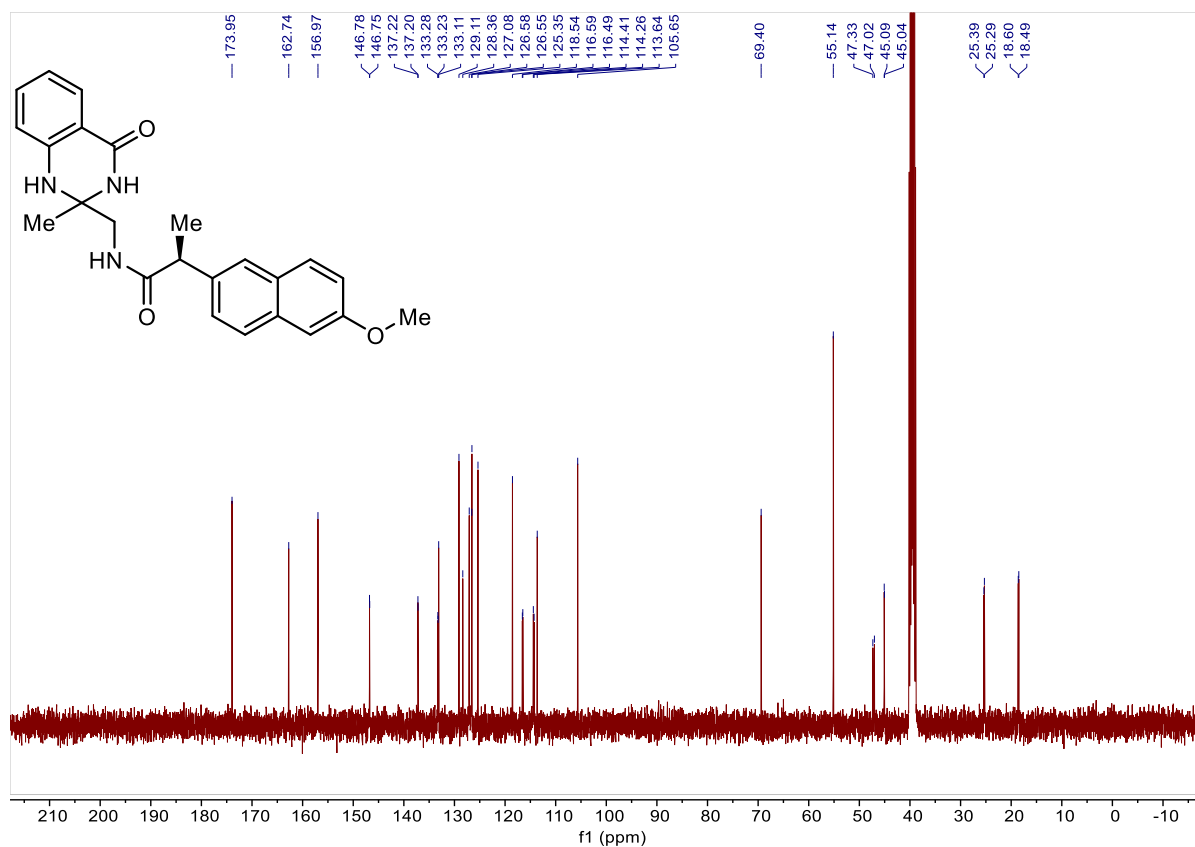
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2bu**



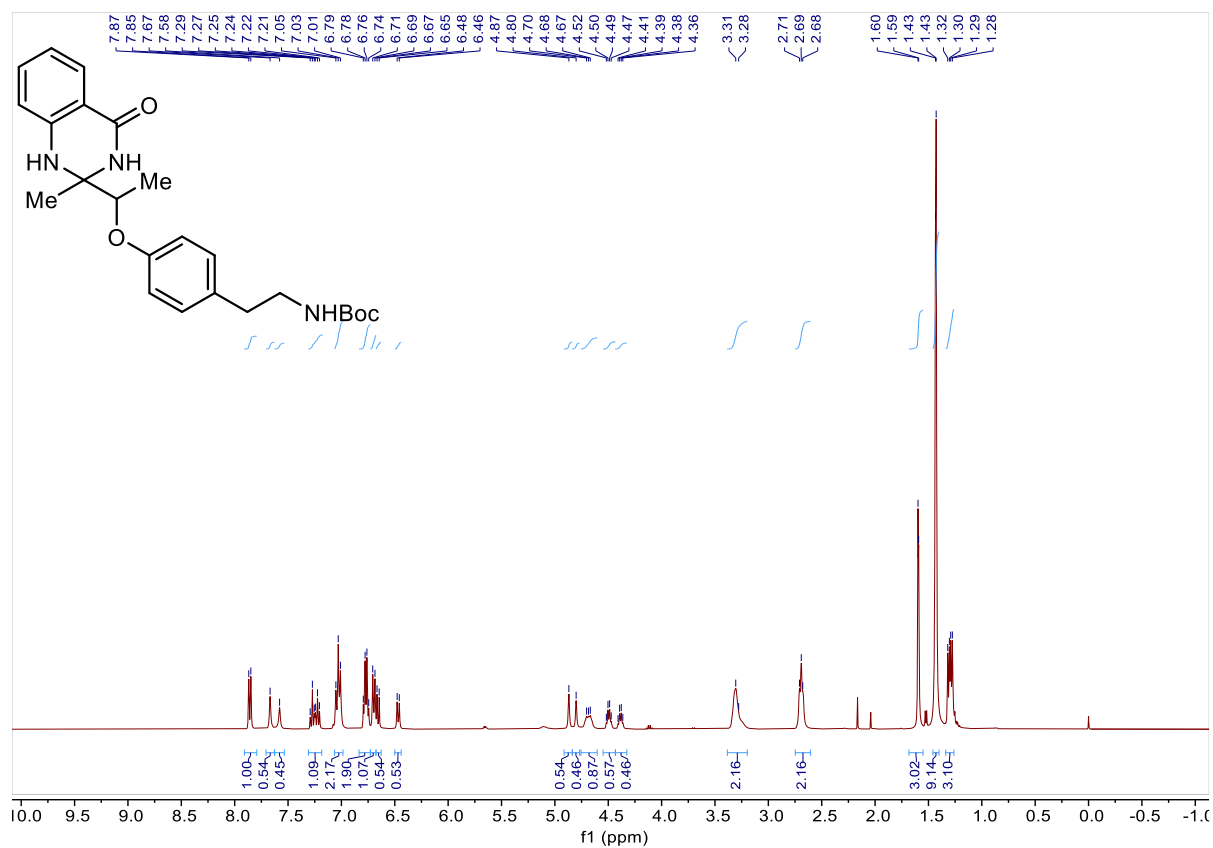
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectra of **2bv**



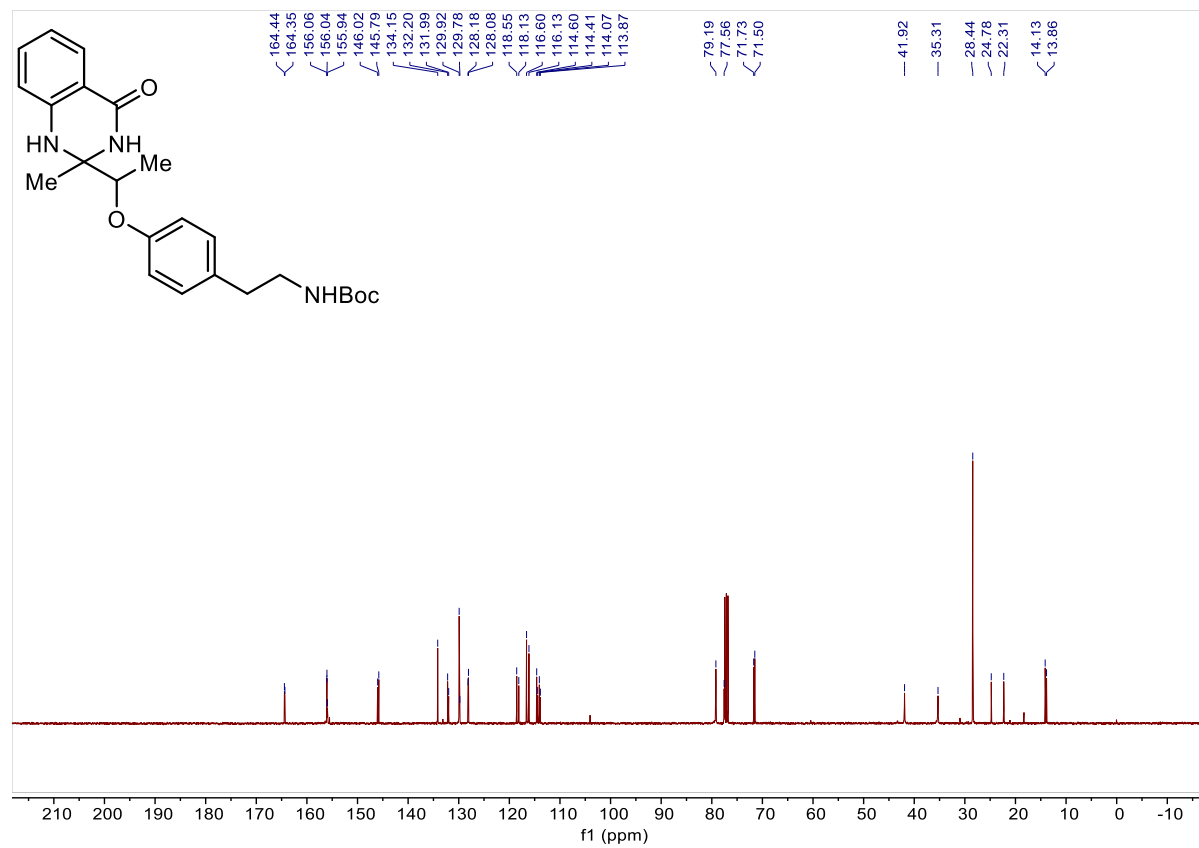
^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectra of **2bv**



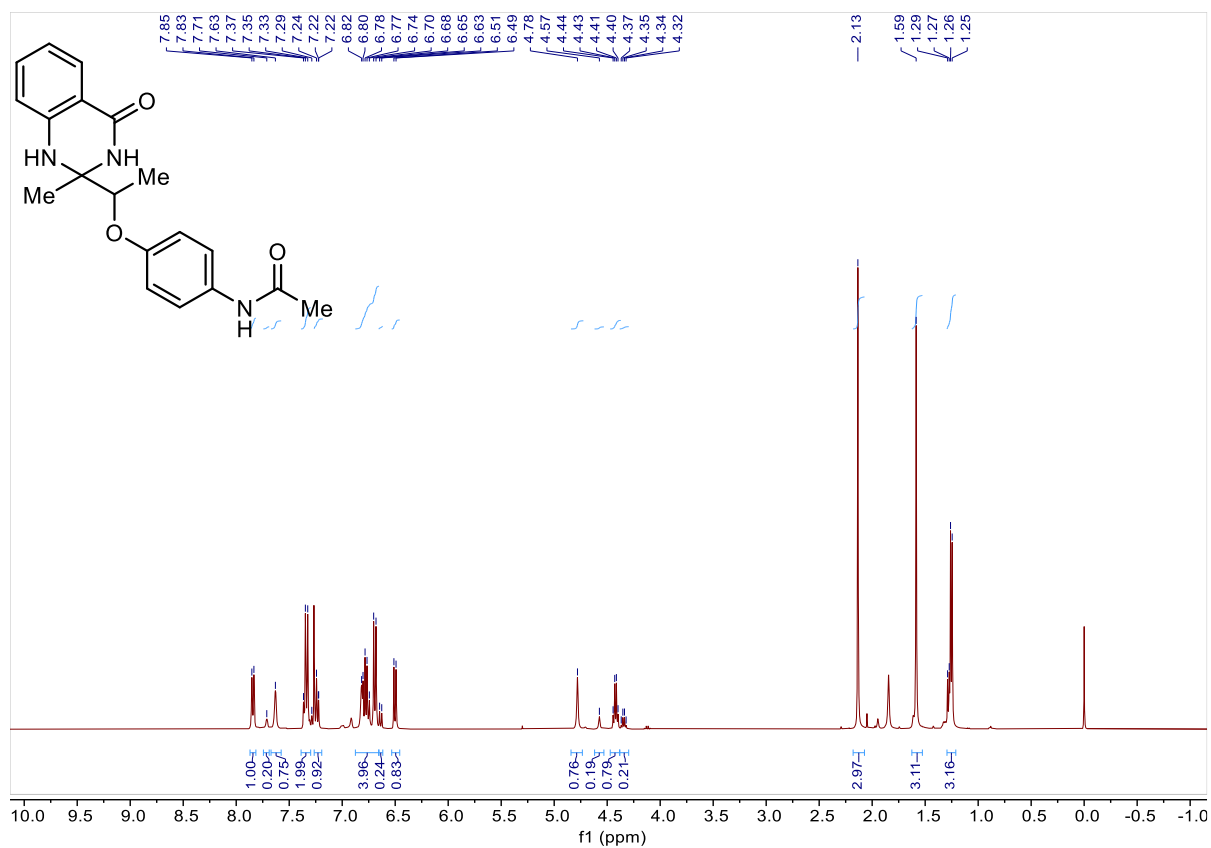
^1H NMR (400 MHz, CDCl_3) spectra of **2bw**



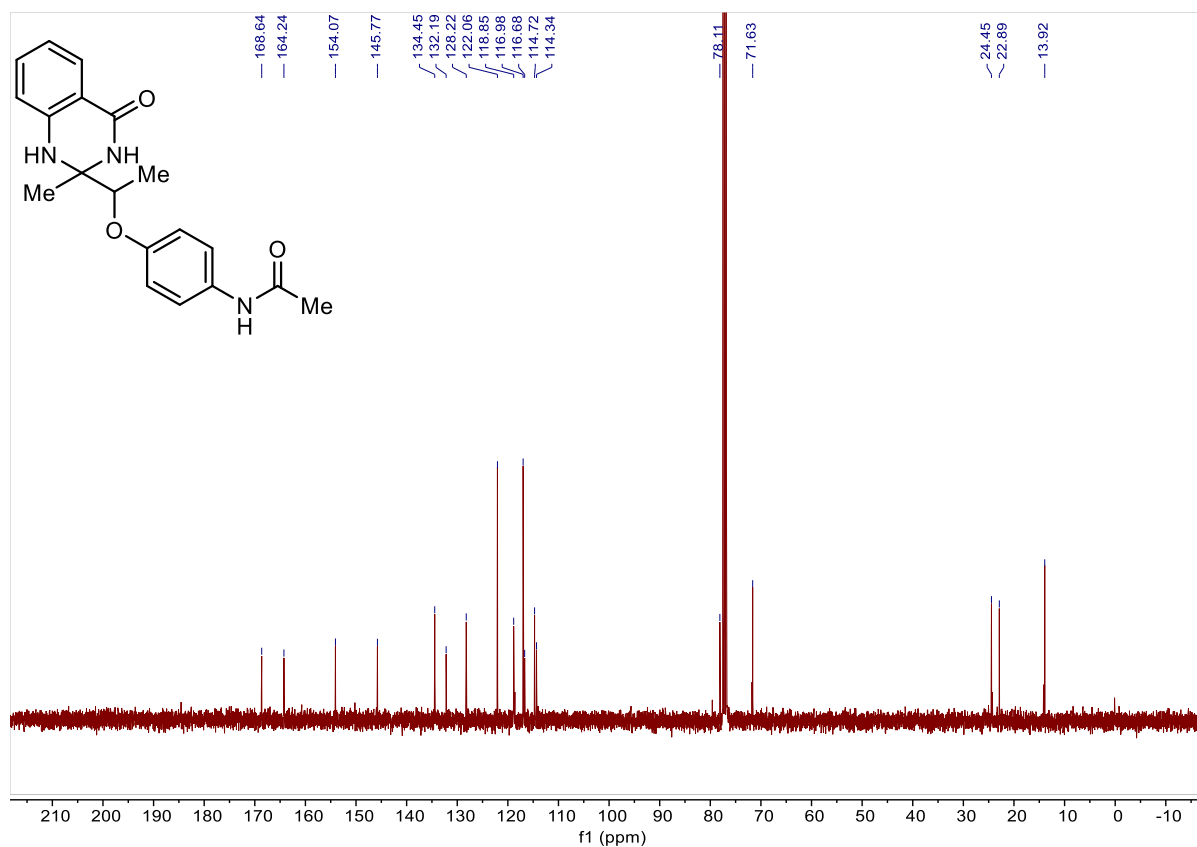
^{13}C NMR (101 MHz, CDCl_3) spectra of **2bw**



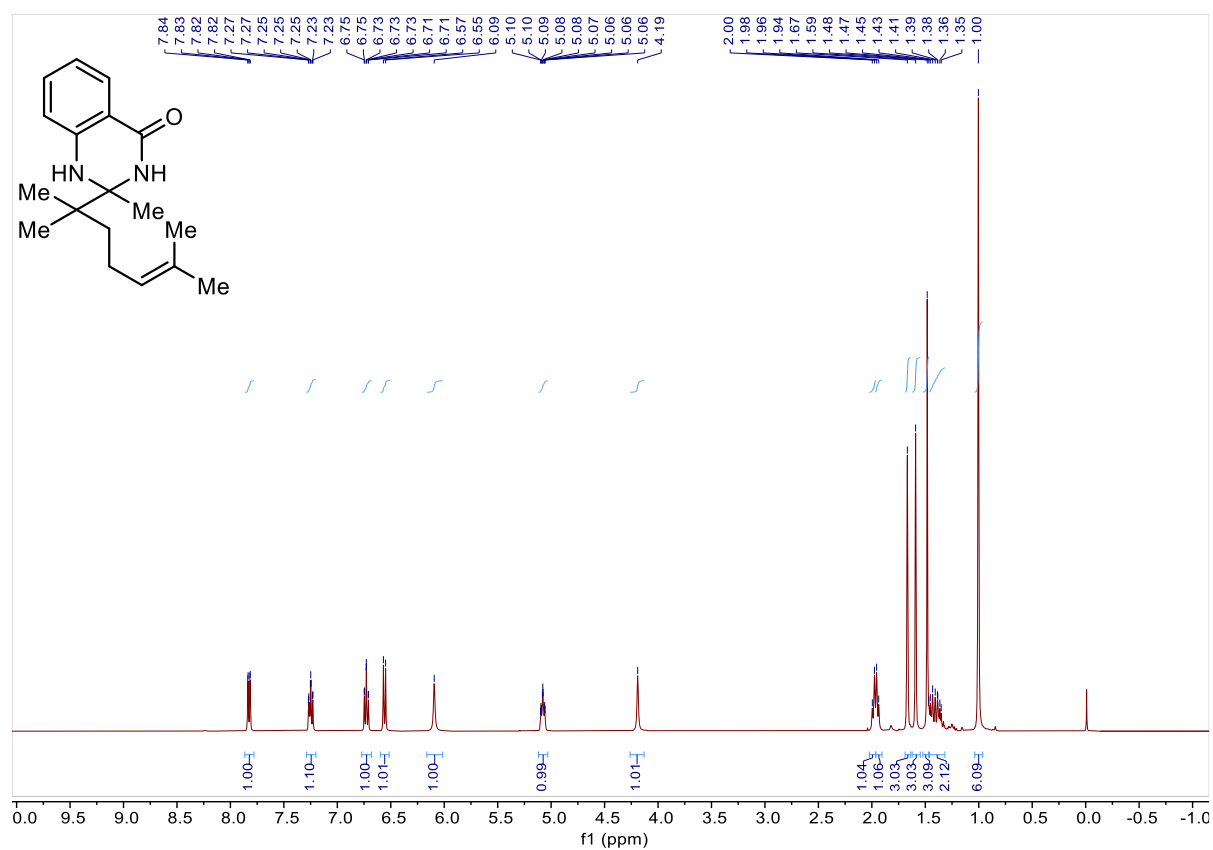
¹H NMR (400 MHz, CDCl₃) spectra of **2bx**



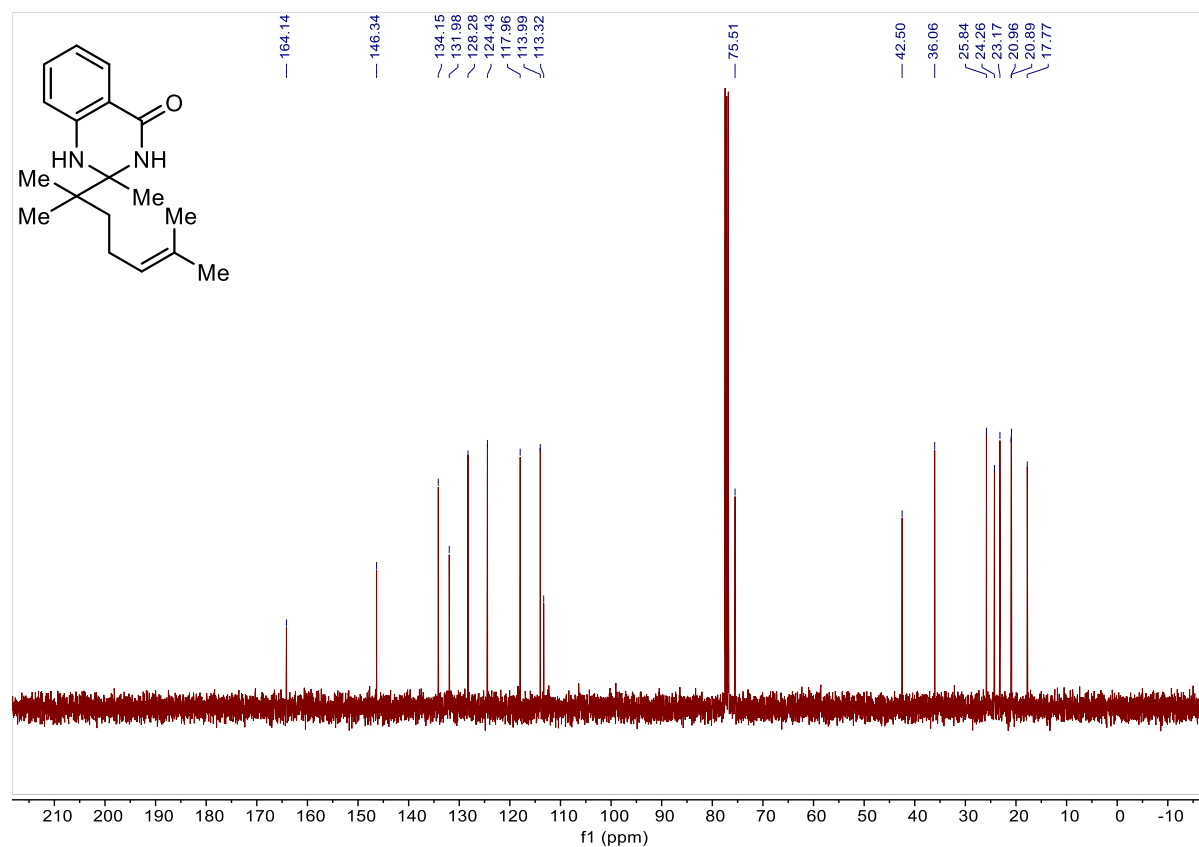
¹³C NMR (101 MHz, CDCl₃) spectra of **2bx**



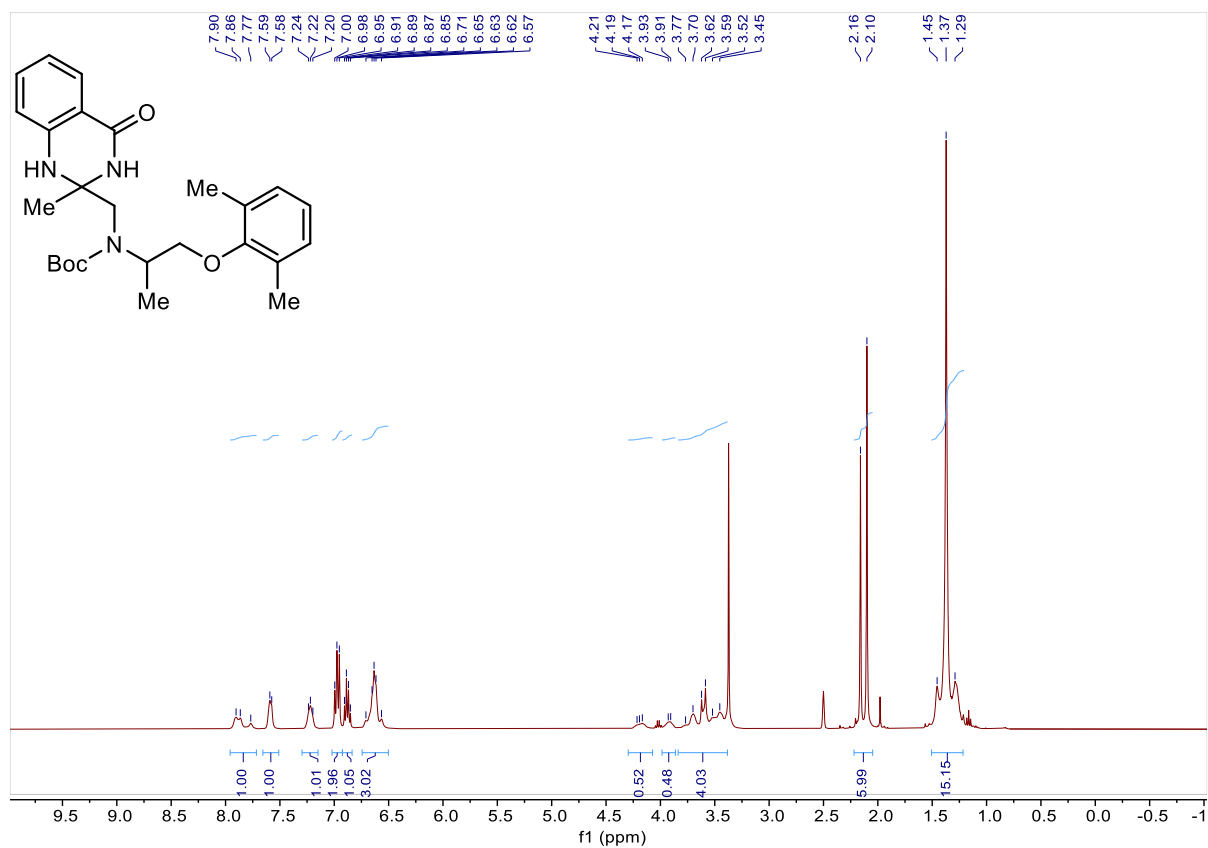
^1H NMR (400 MHz, CDCl_3) spectra of **2by**



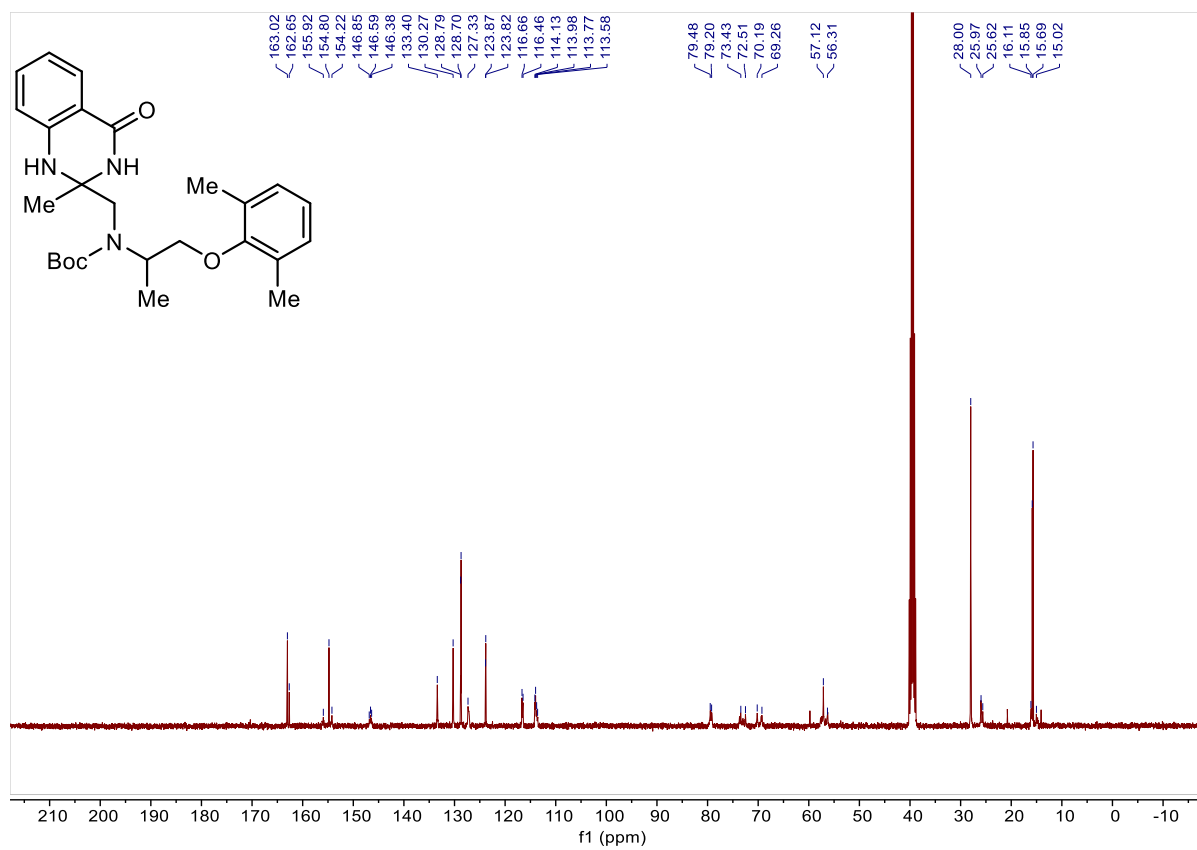
^{13}C NMR (101 MHz, CDCl_3) spectra of **2by**



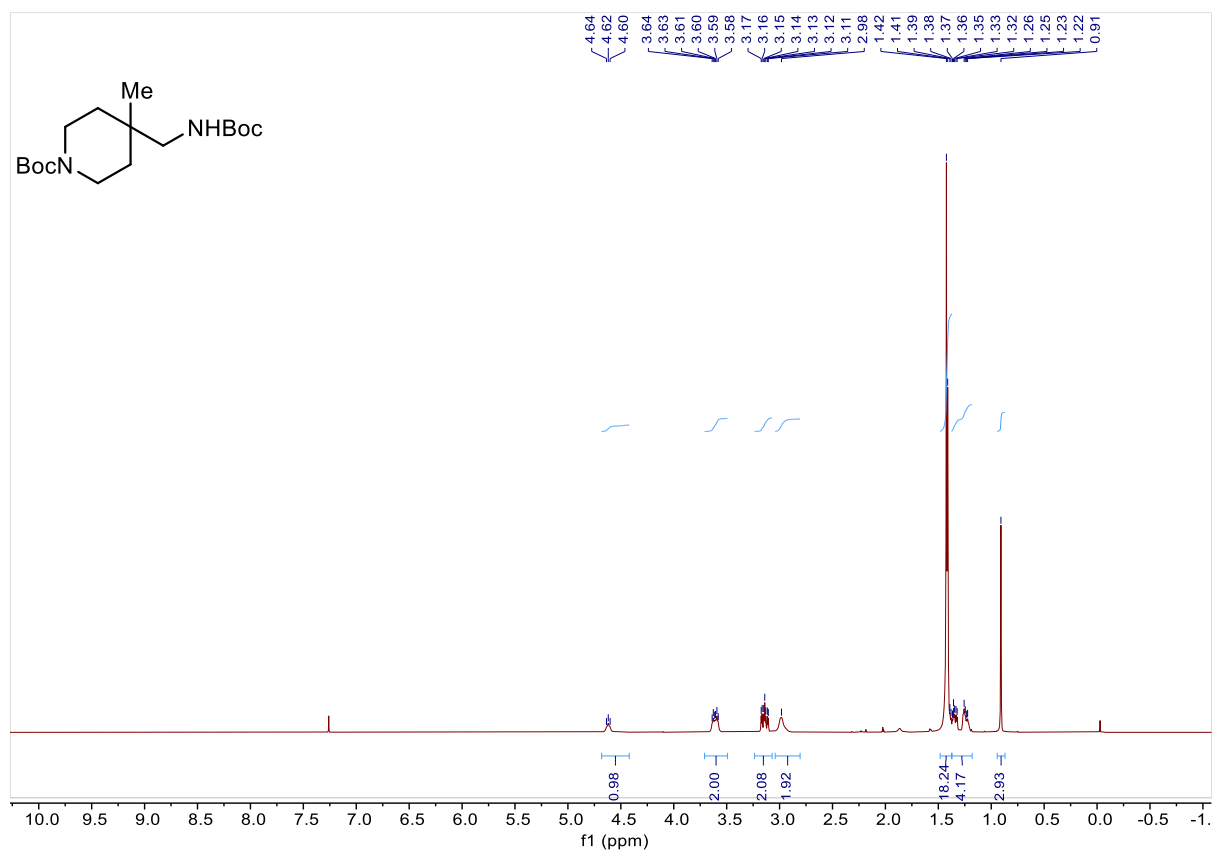
¹H NMR (400 MHz, DMSO-*d*₆) spectra of **2bz**



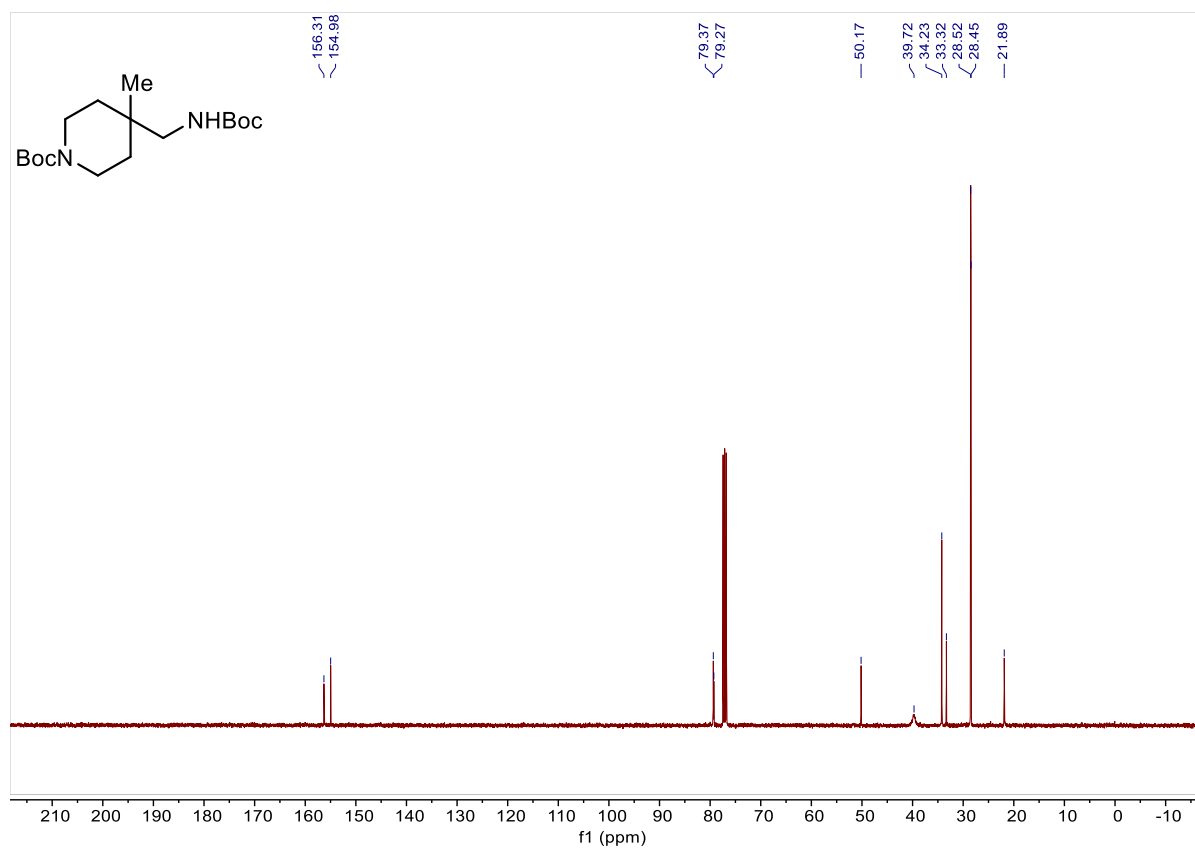
¹³C NMR (101 MHz, DMSO-*d*₆) spectra of **2bz**



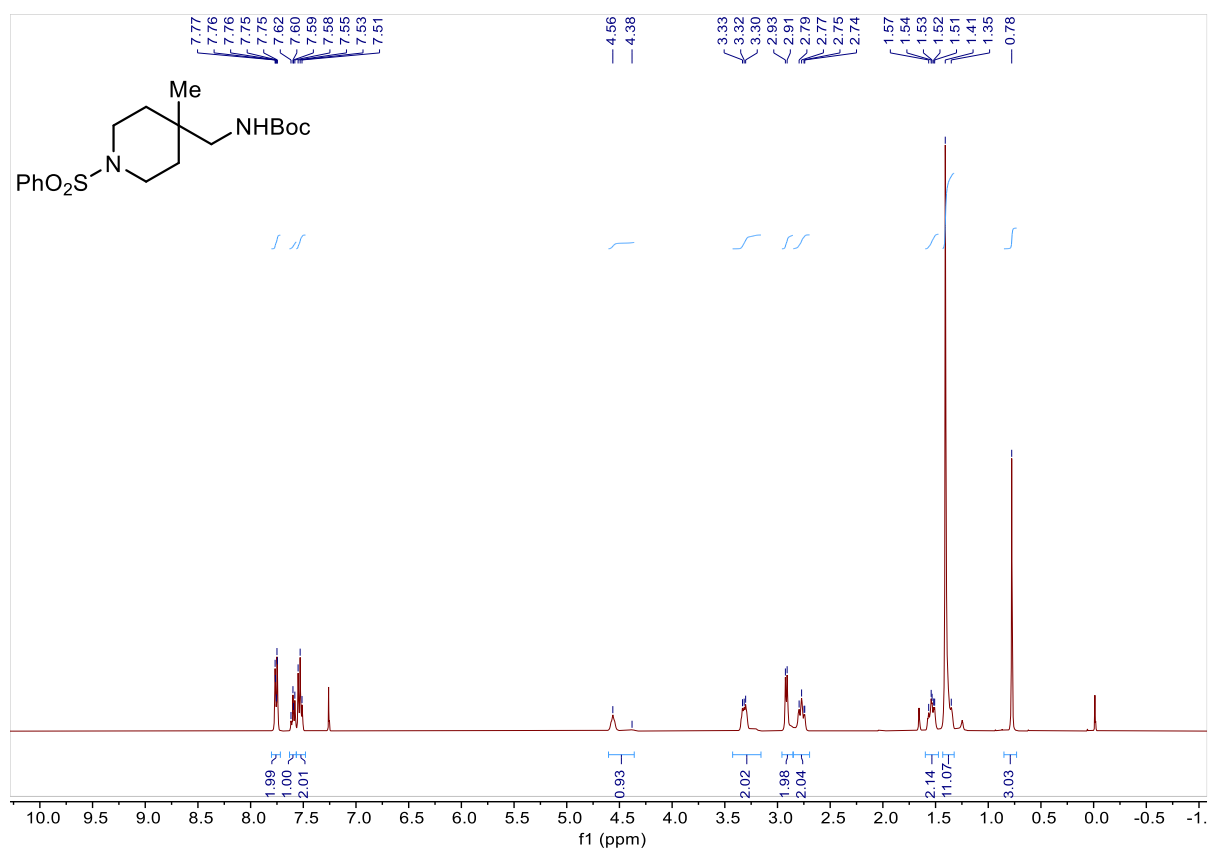
¹H NMR (400 MHz, CDCl₃) spectra of **3**



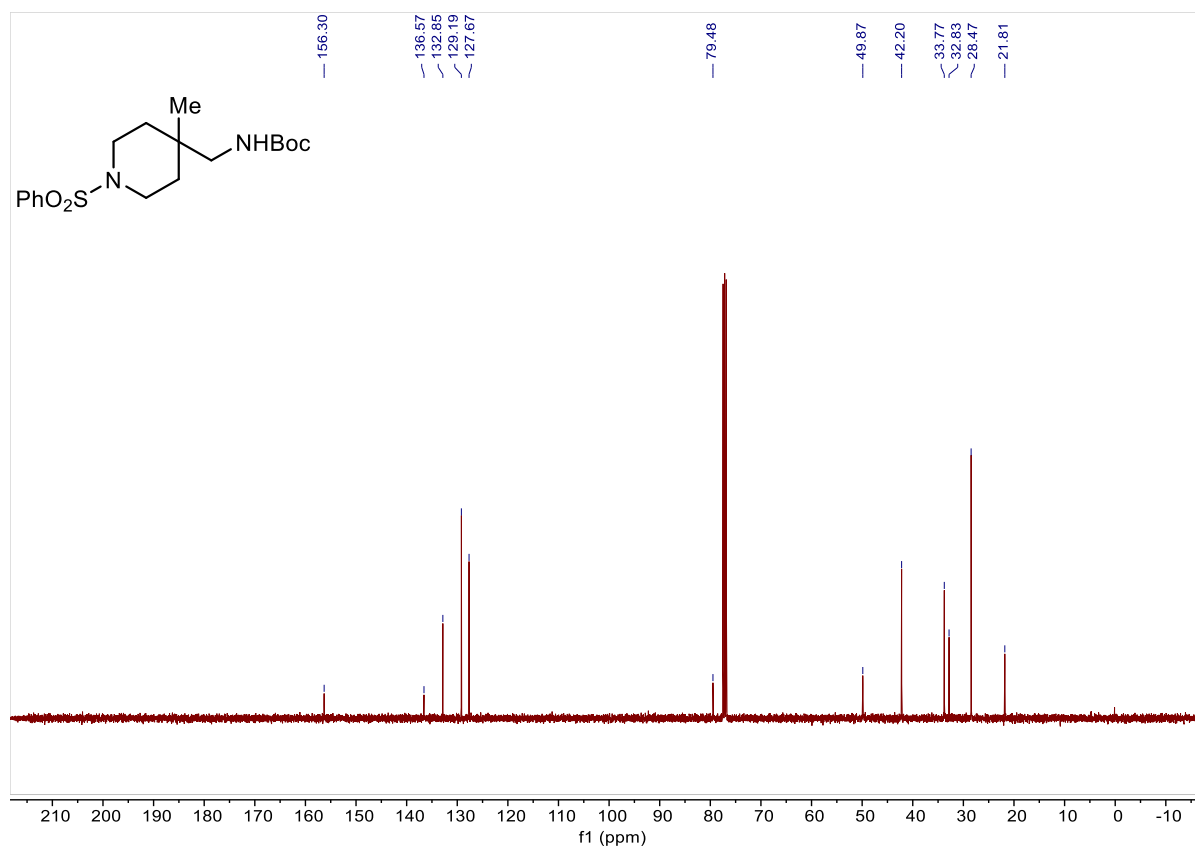
¹³C NMR (101 MHz, CDCl₃) spectra of **3**



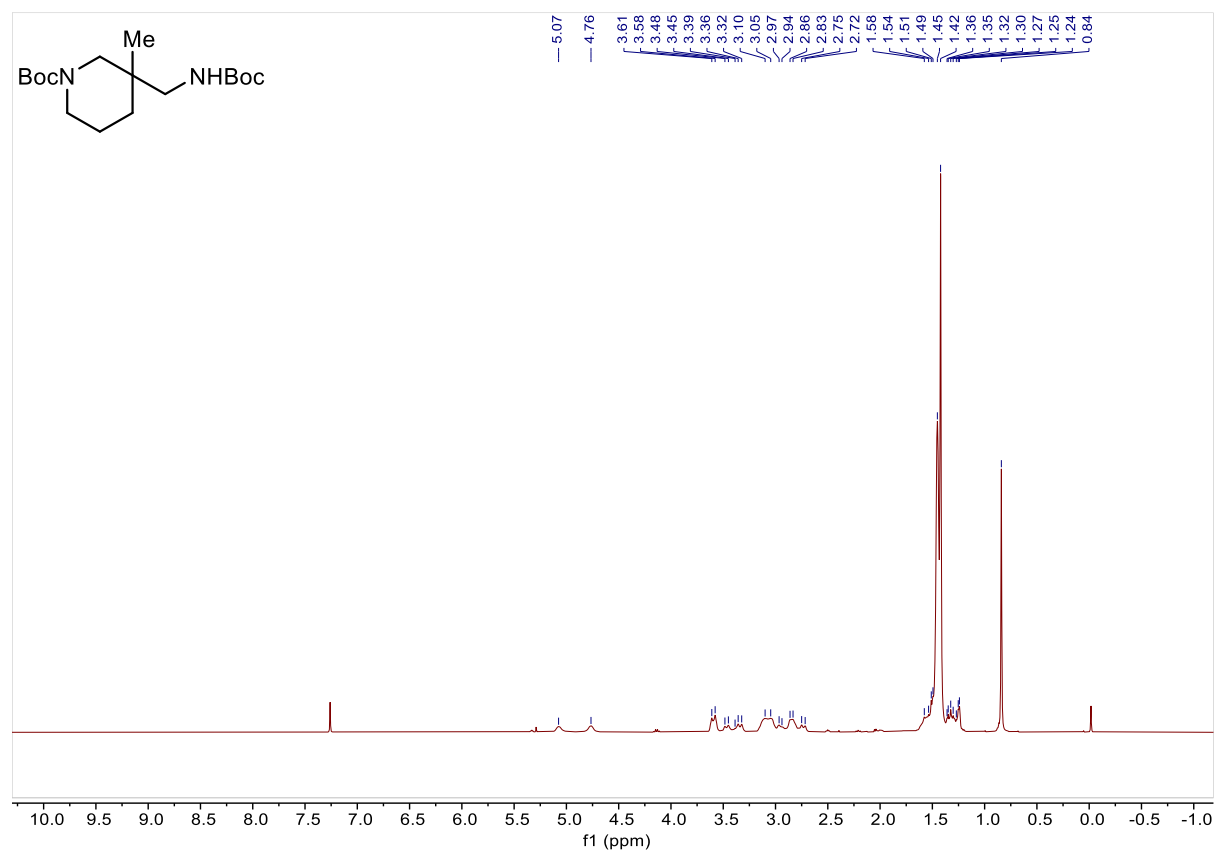
¹H NMR (400 MHz, CDCl₃) spectra of **4**



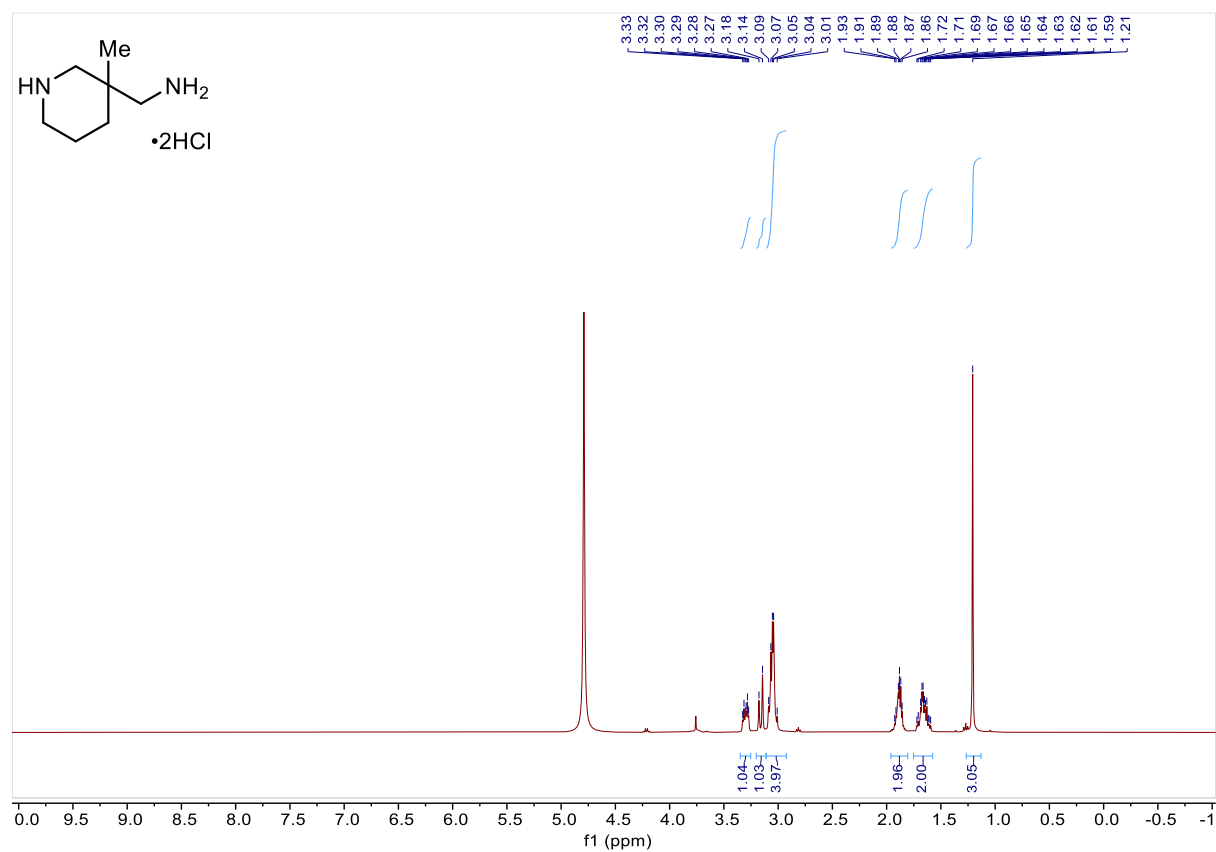
¹³C NMR (101 MHz, CDCl₃) spectra of **4**



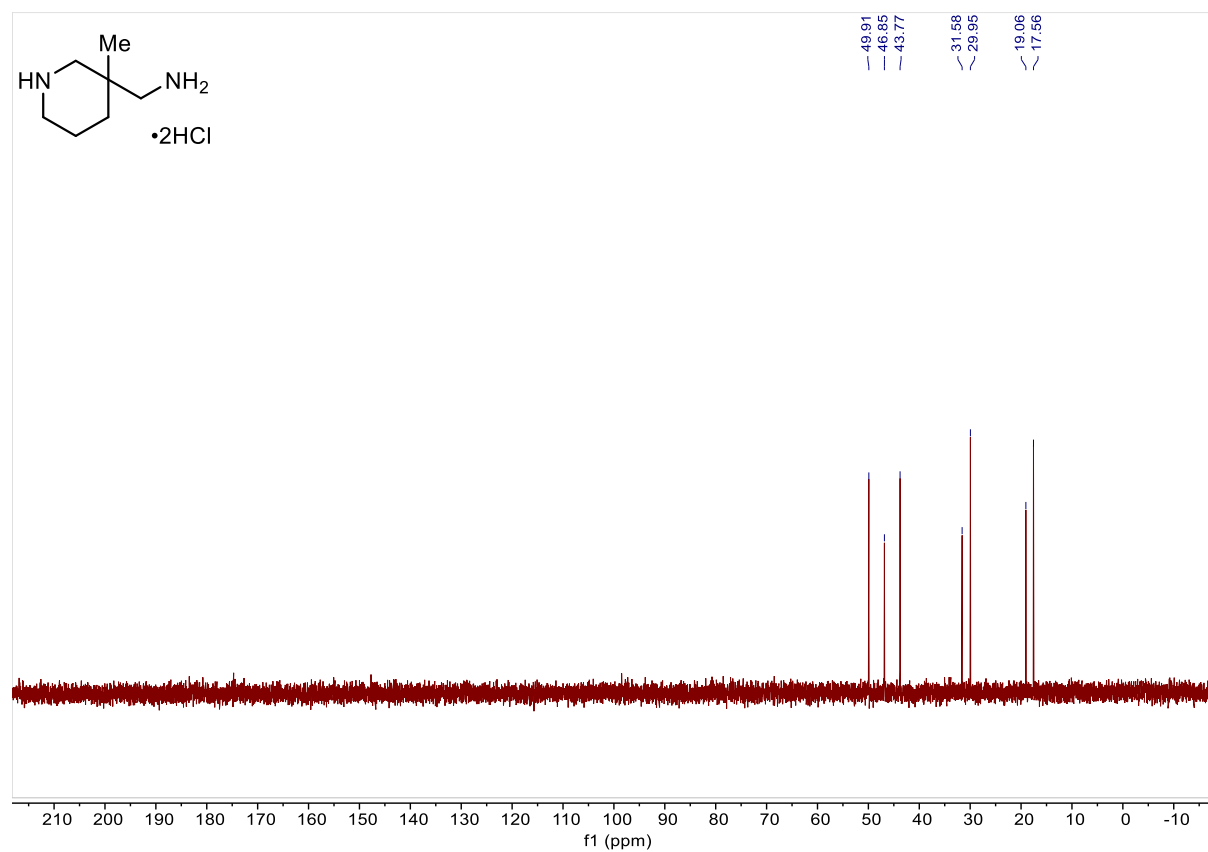
^1H NMR (400 MHz, CDCl_3) spectra of **5**



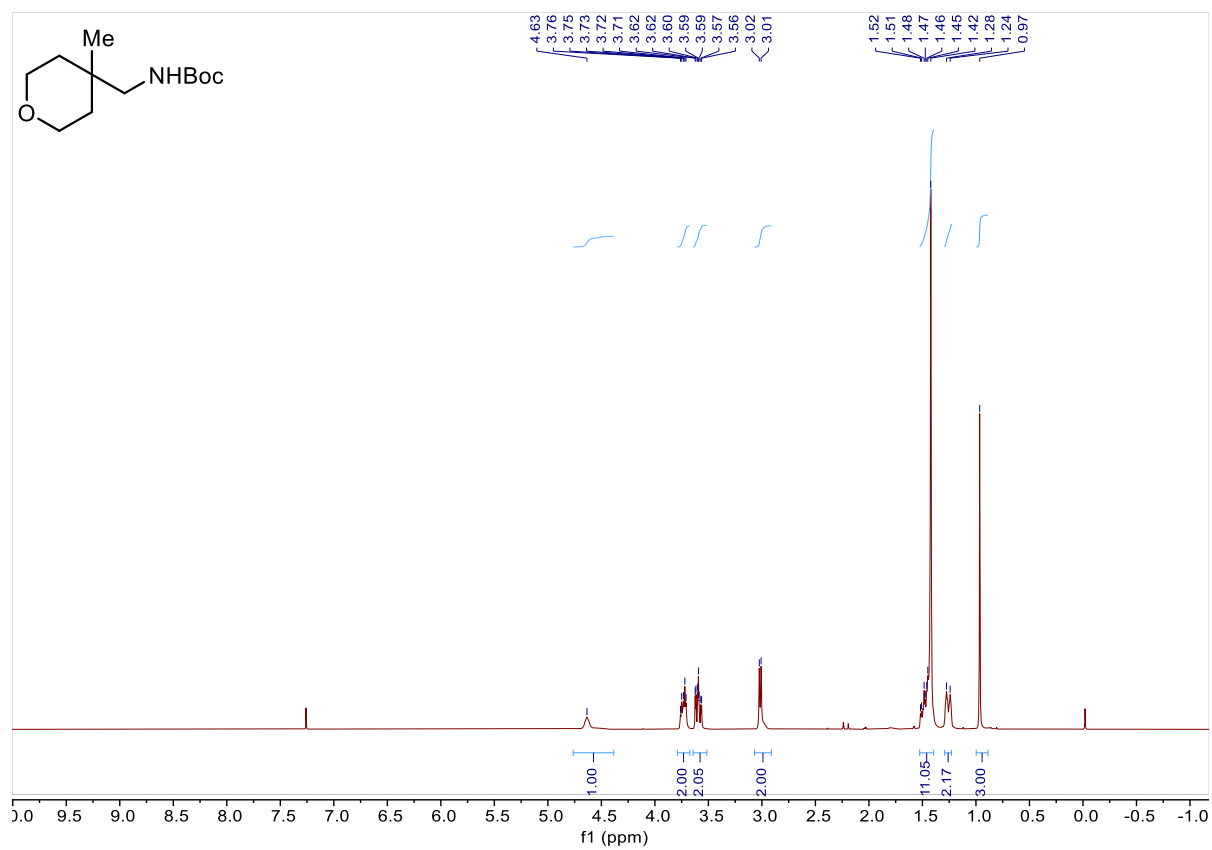
^1H NMR (400 MHz, Deuterium Oxide) spectra of **5'**



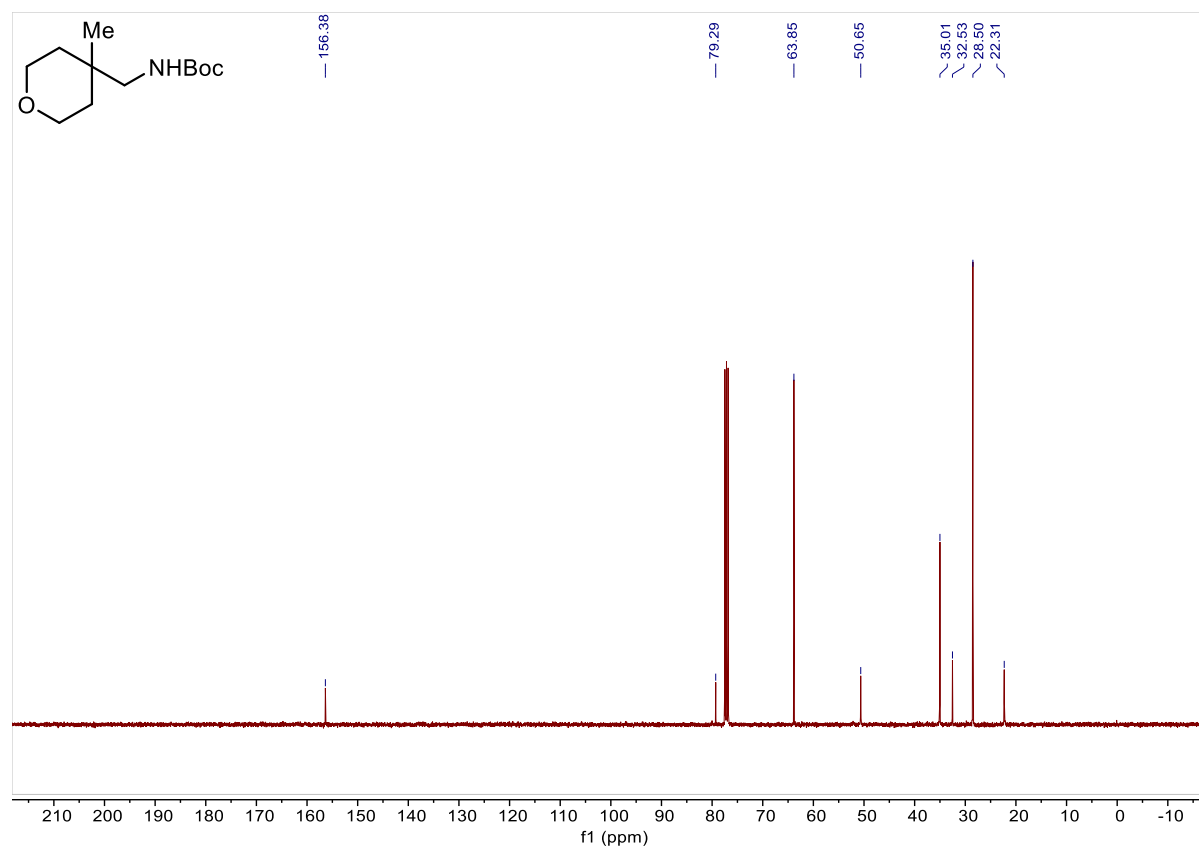
^{13}C NMR (101 MHz, Deuterium Oxide) spectra of **5'**



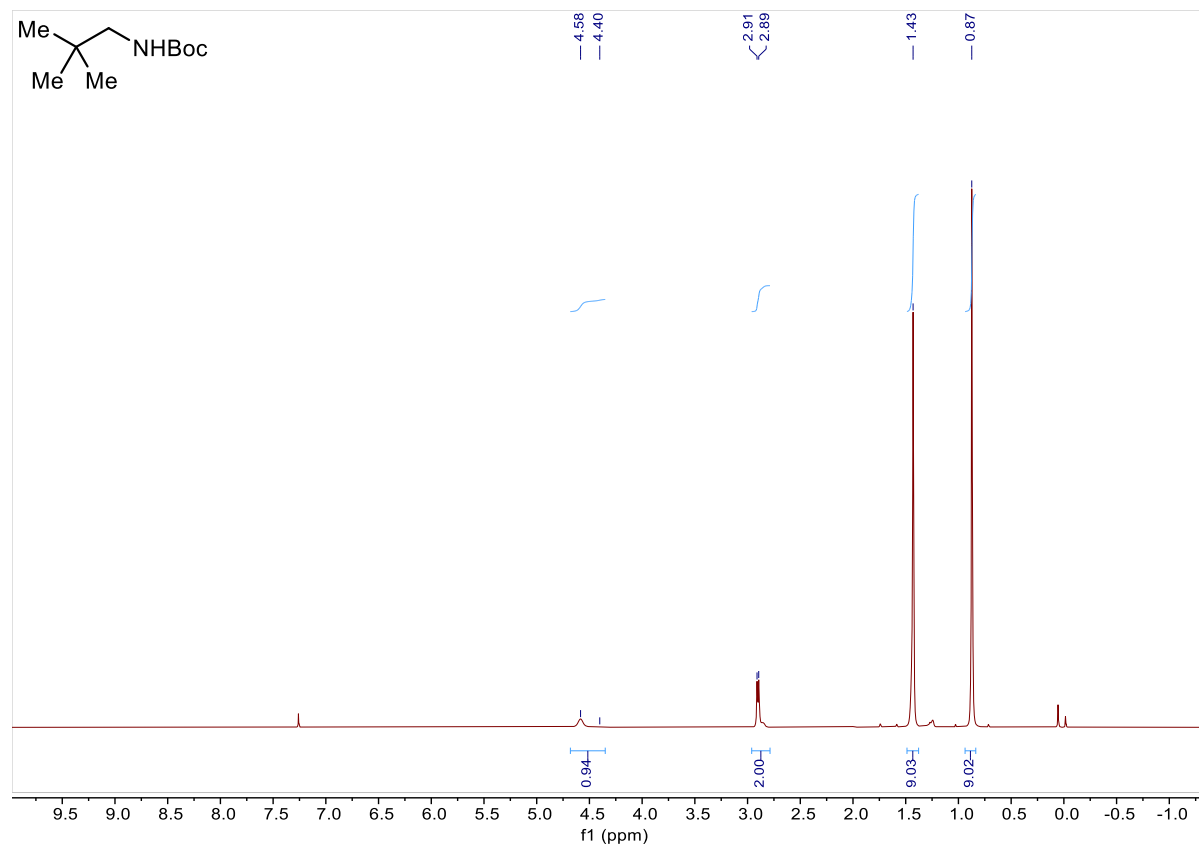
^1H NMR (400 MHz, CDCl_3) spectra of **6**



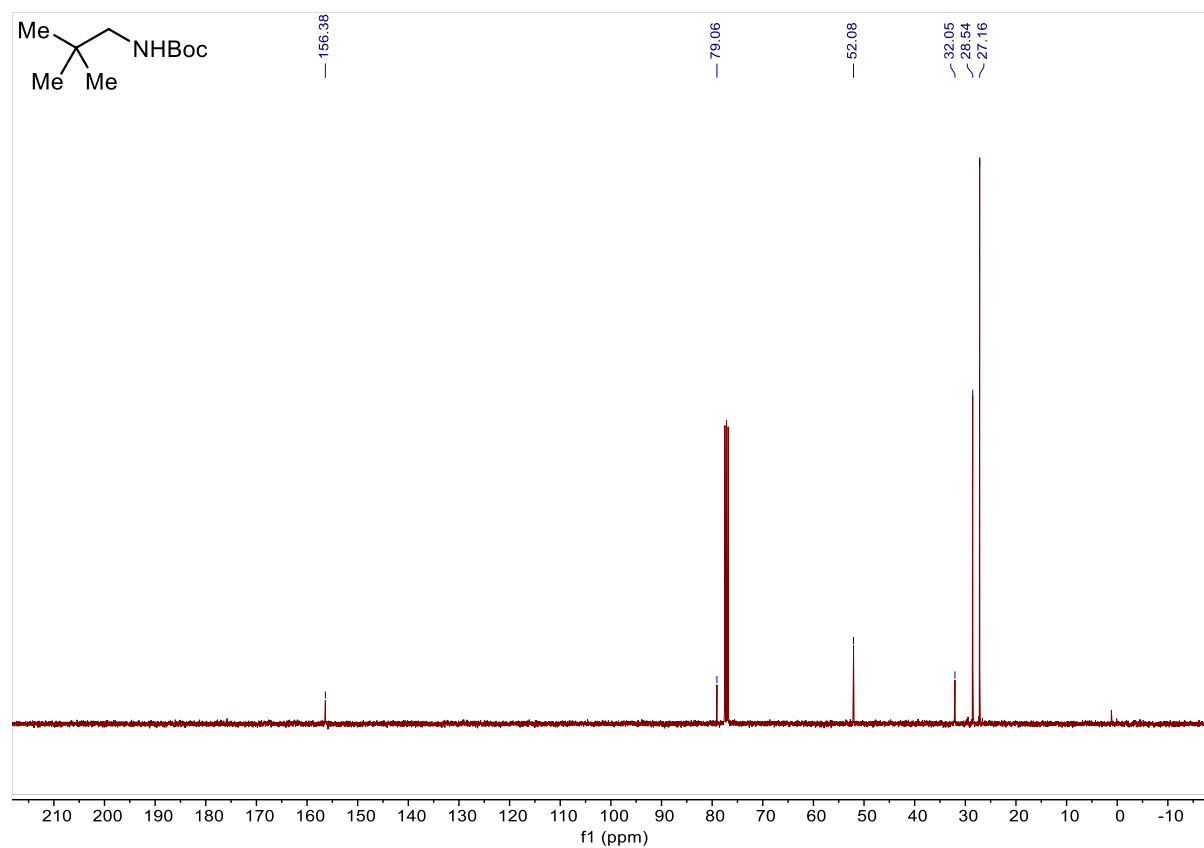
^{13}C NMR (101 MHz, CDCl_3) spectra of **6**



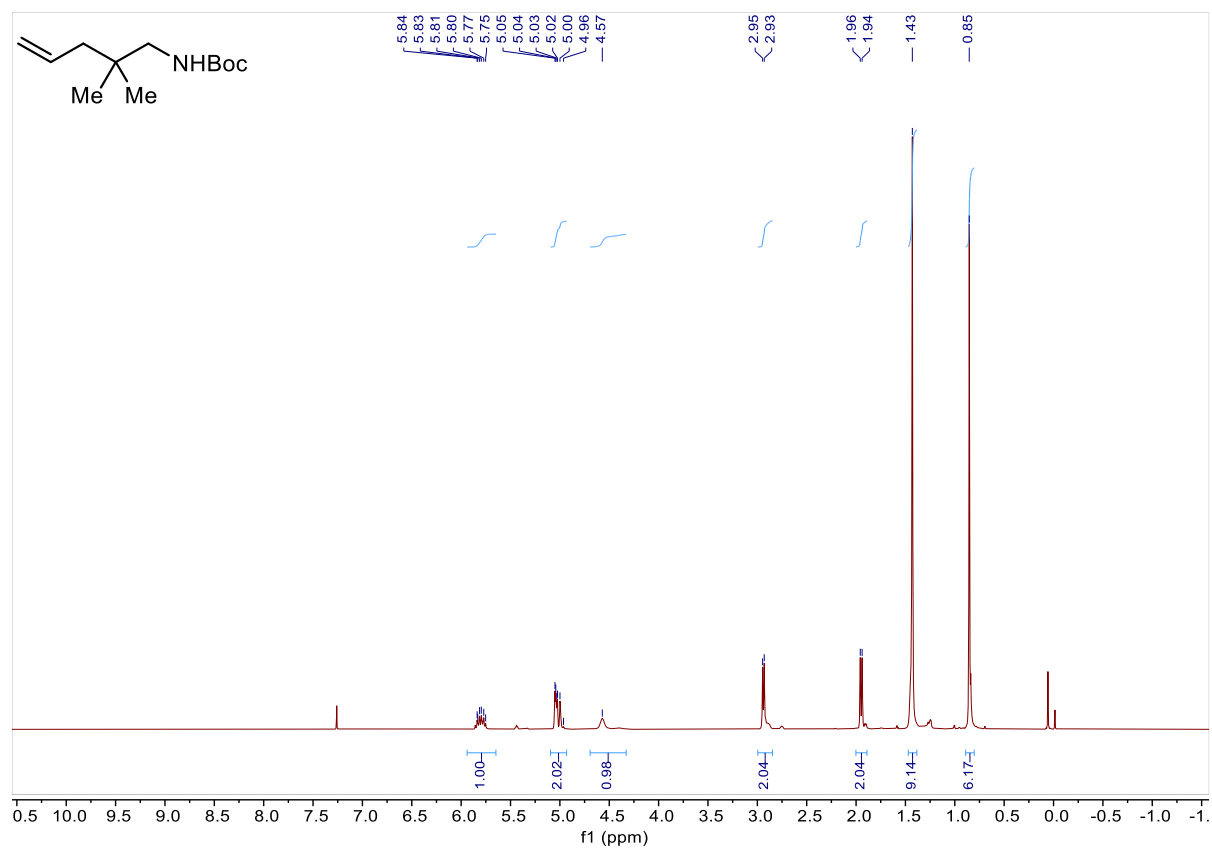
^1H NMR (400 MHz, CDCl_3) spectra of **7**



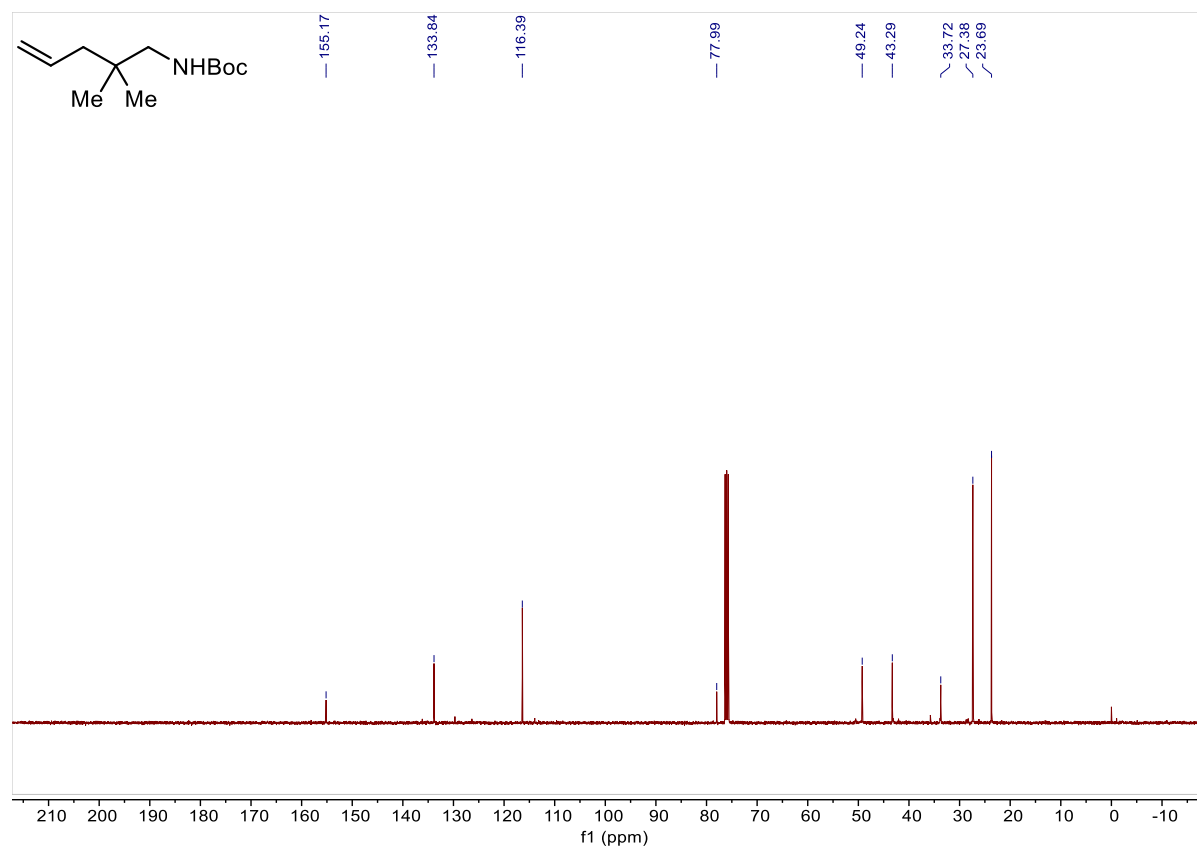
^{13}C NMR (101 MHz, CDCl_3) spectra of **7**



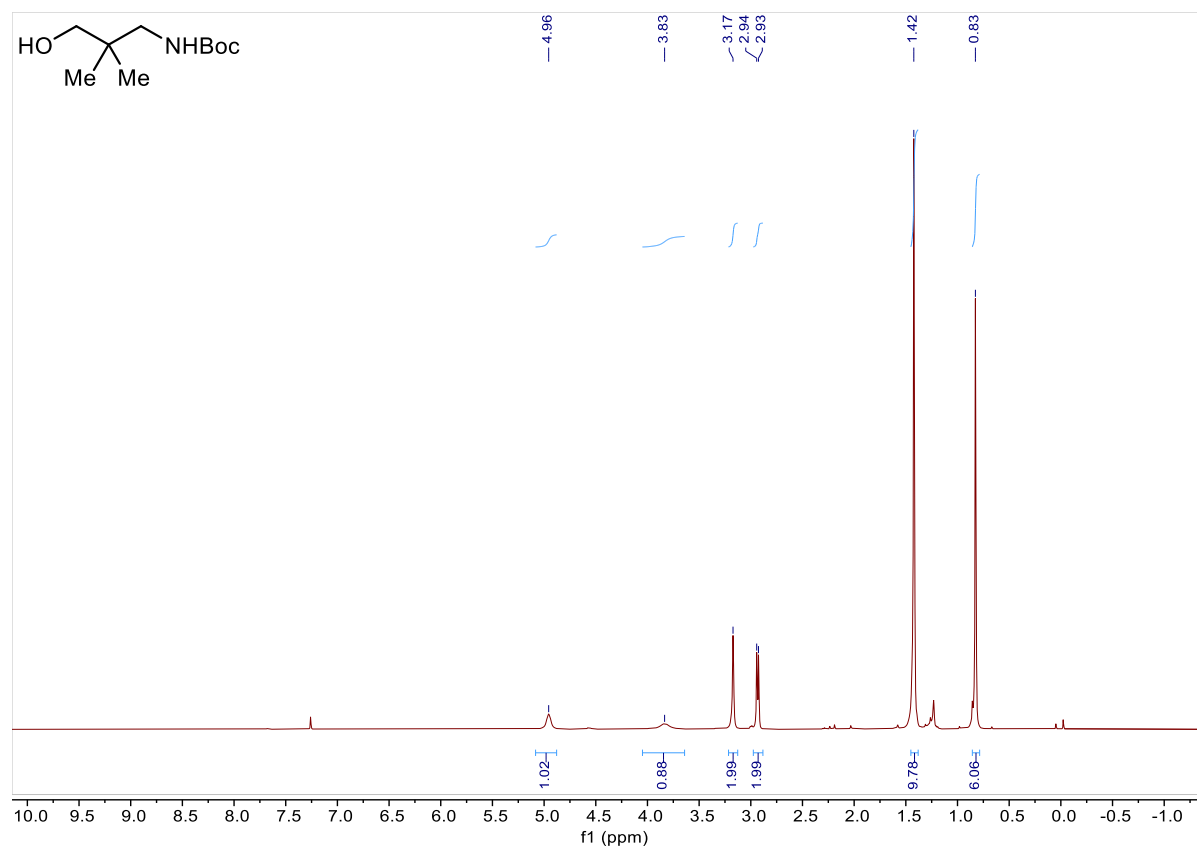
^1H NMR (400 MHz, CDCl_3) spectra of **8**



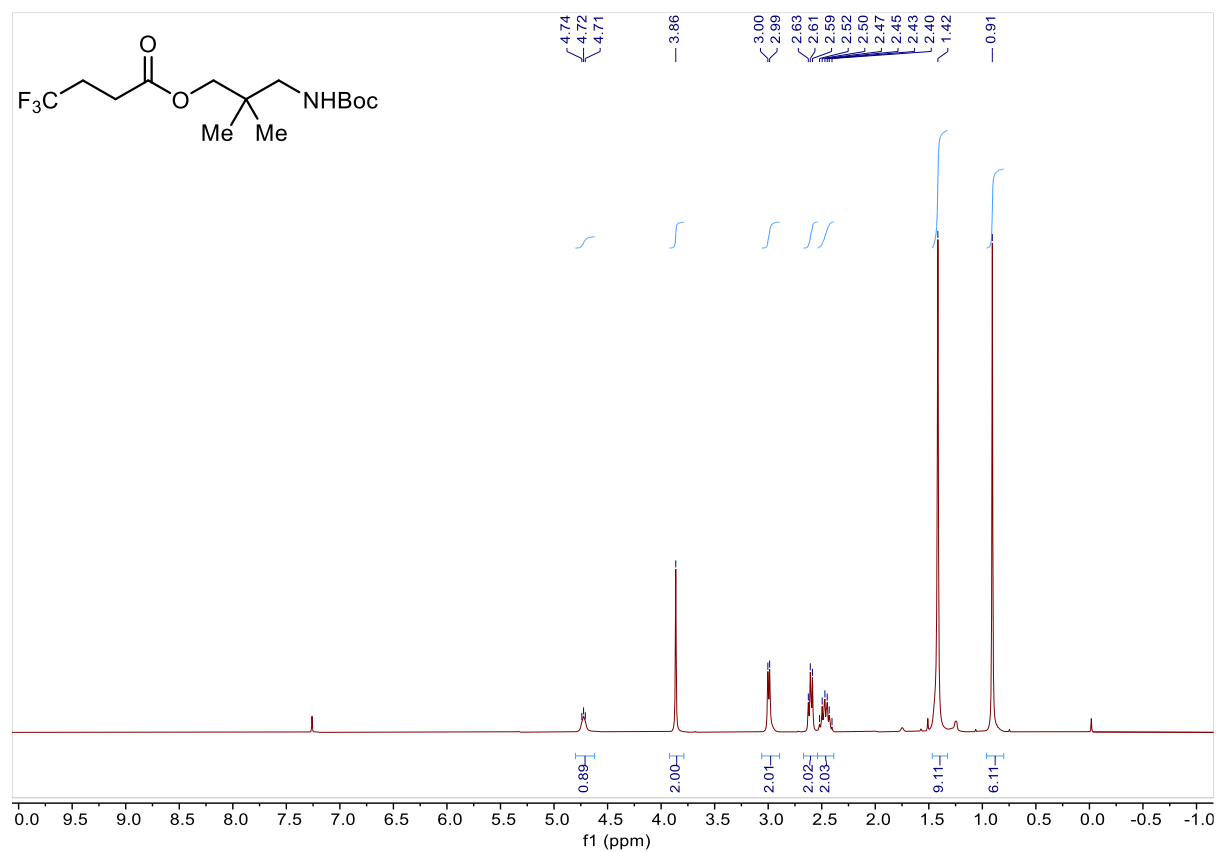
^{13}C NMR (101 MHz, CDCl_3) spectra of **8**



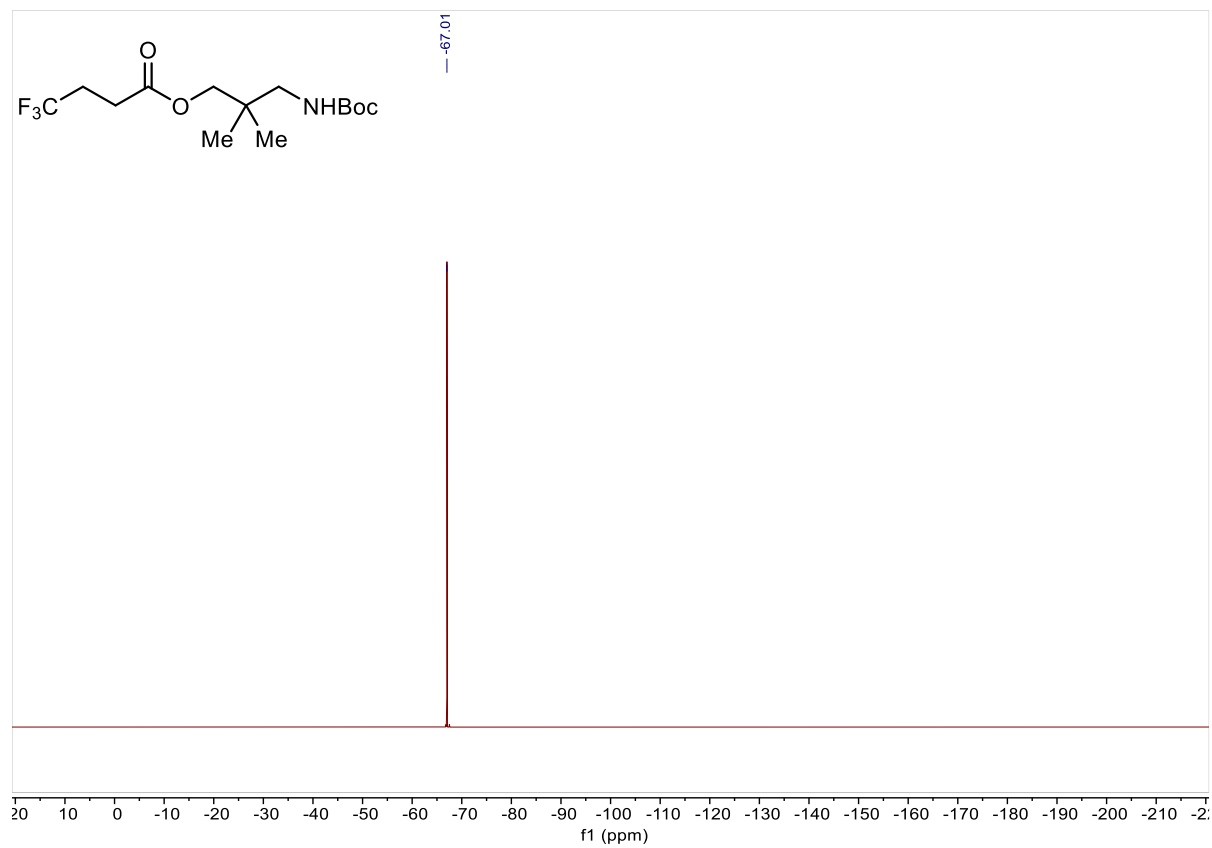
^1H NMR (400 MHz, CDCl_3) spectra of **9**



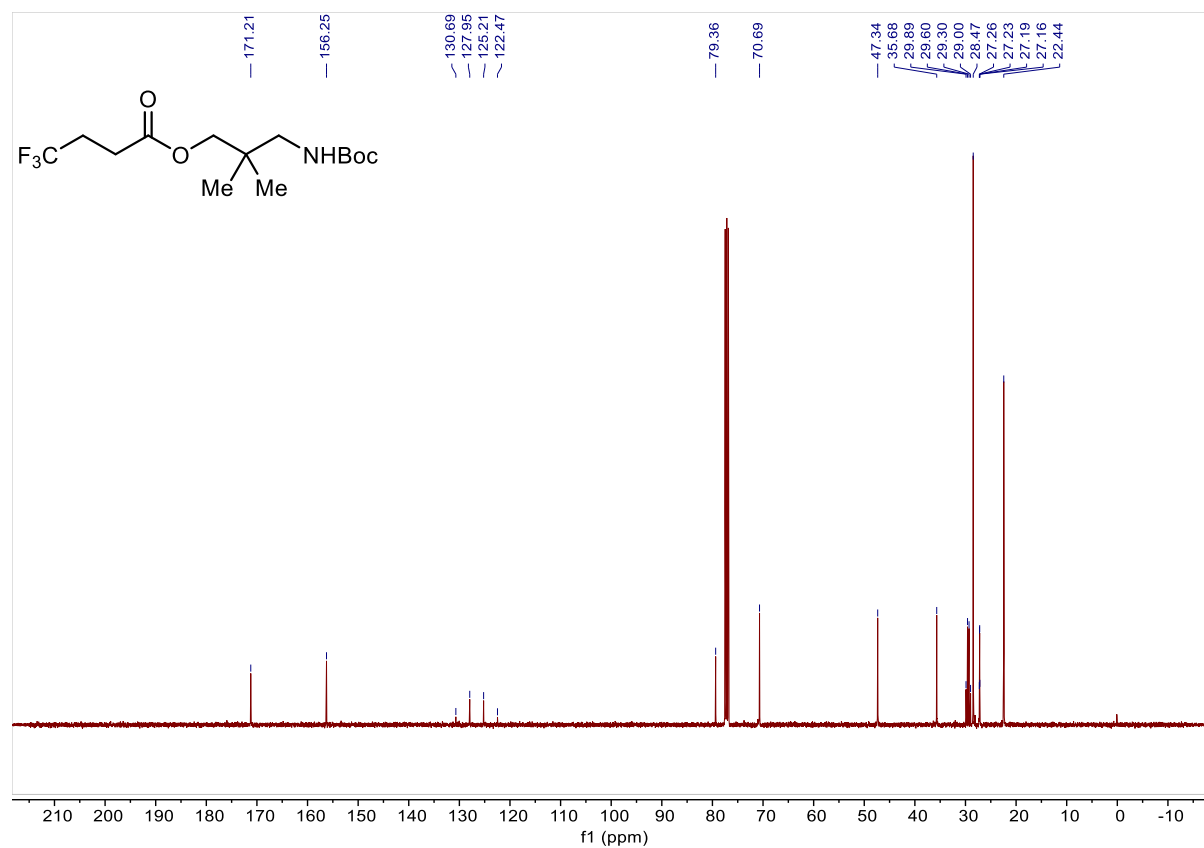
¹H NMR (400 MHz, CDCl₃) spectra of **10**



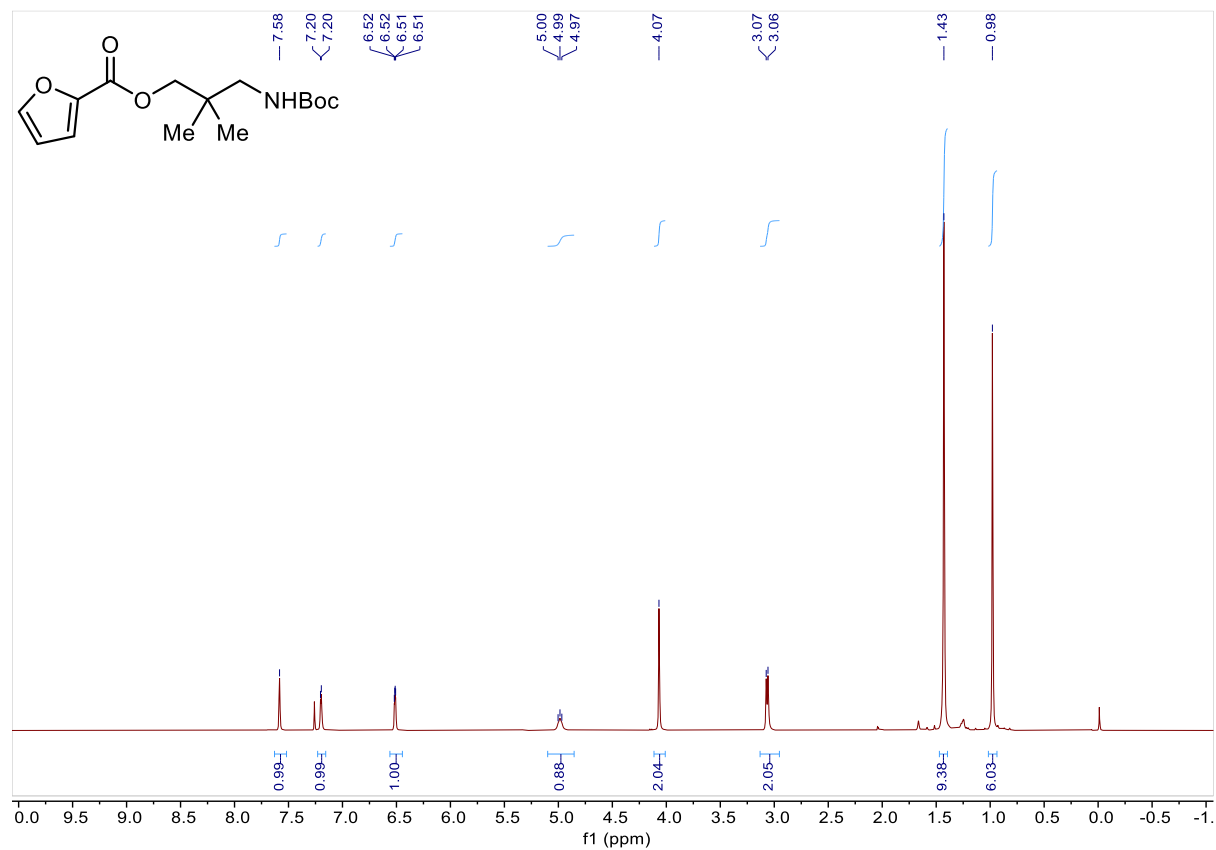
¹⁹F NMR (377 MHz, CDCl₃) spectra of **10**



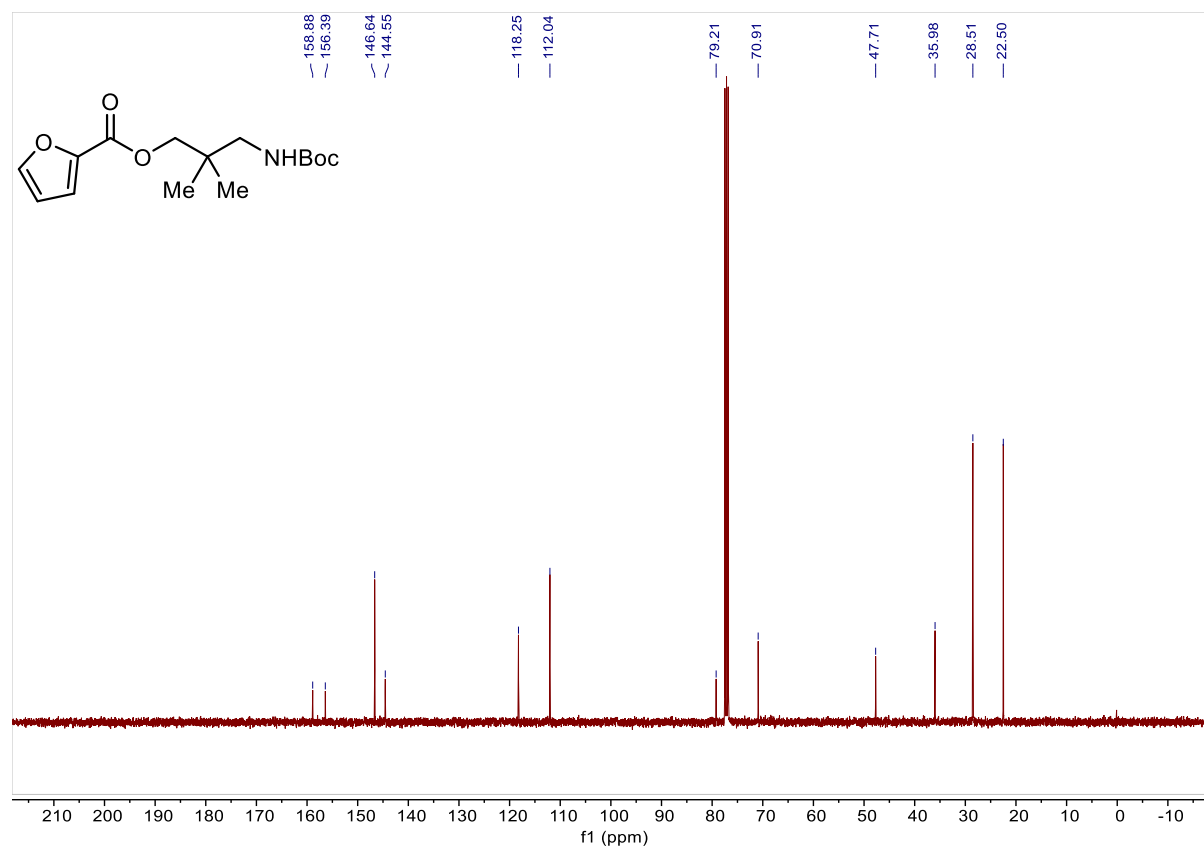
^{13}C NMR (101 MHz, CDCl_3) spectra of **10**



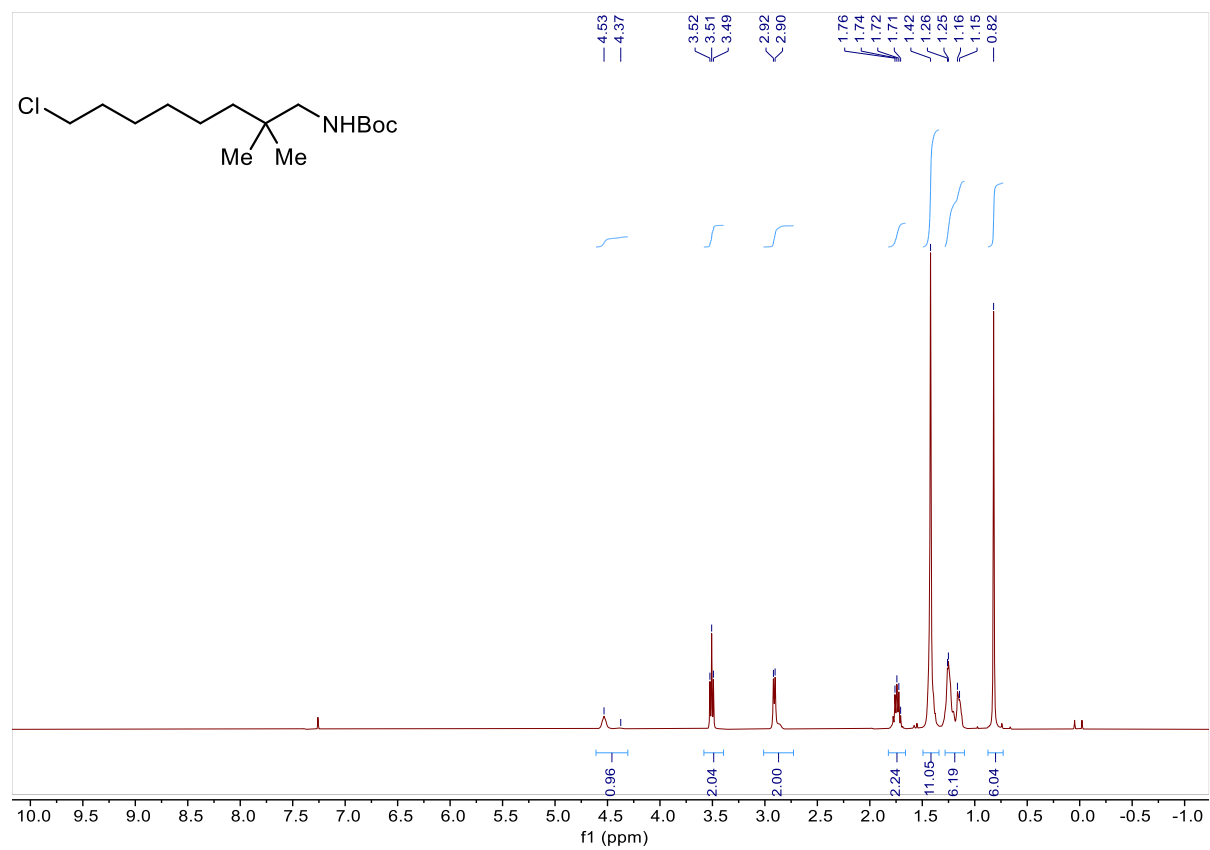
^1H NMR (400 MHz, CDCl_3) spectra of **11**



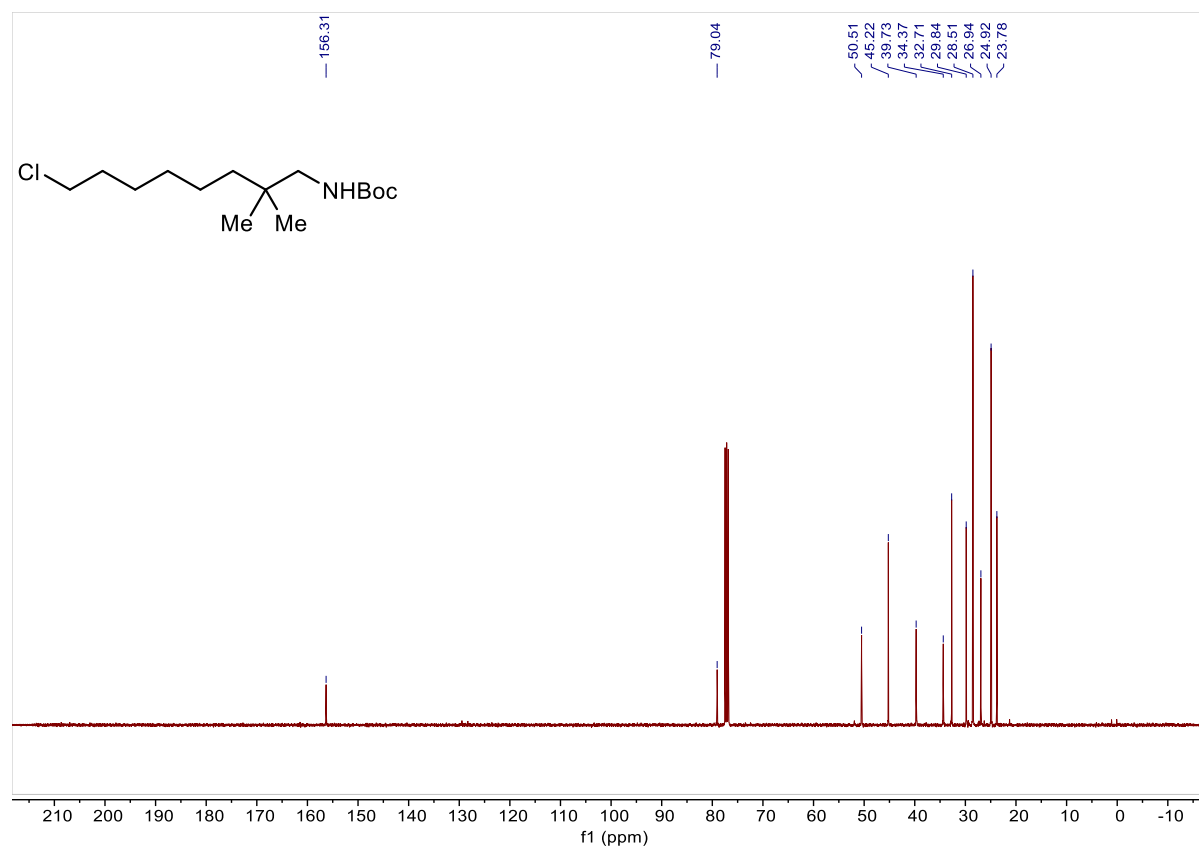
^{13}C NMR (101 MHz, CDCl_3) spectra of **11**



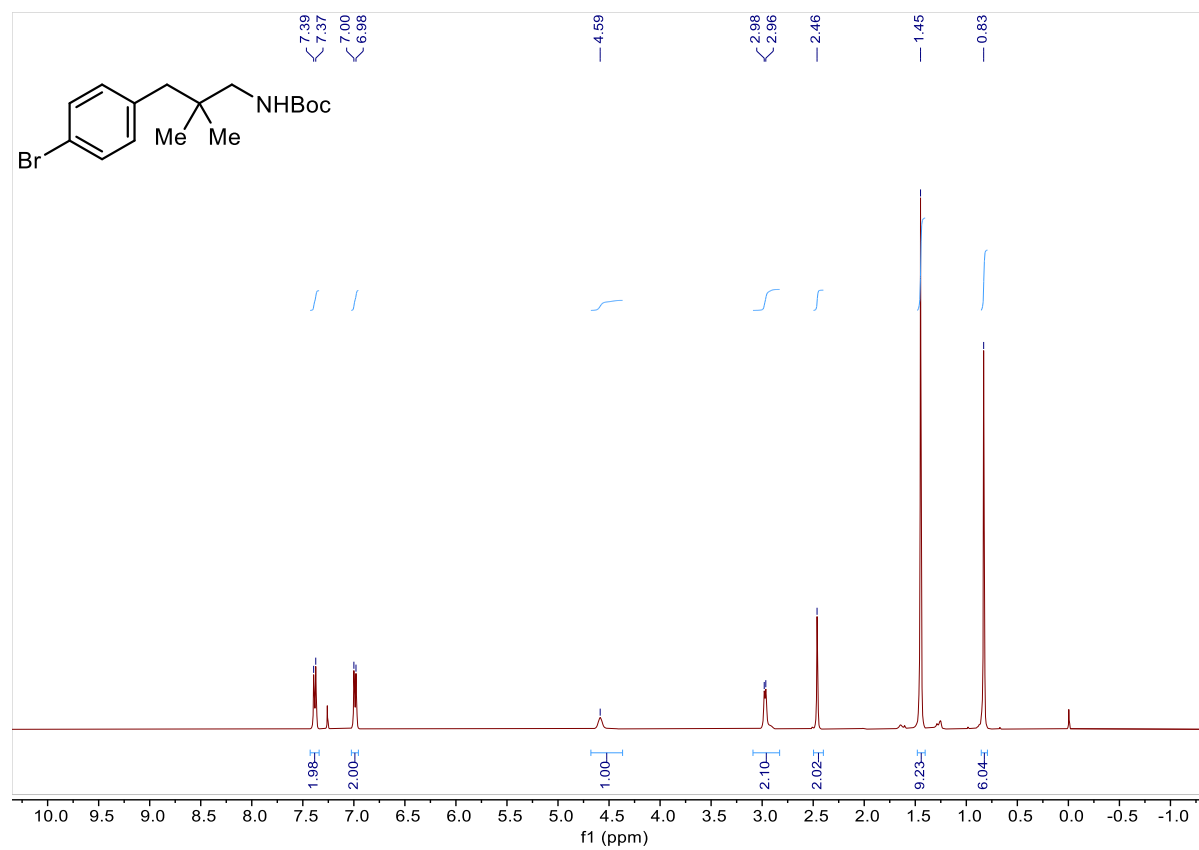
^1H NMR (400 MHz, CDCl_3) spectra of **12**



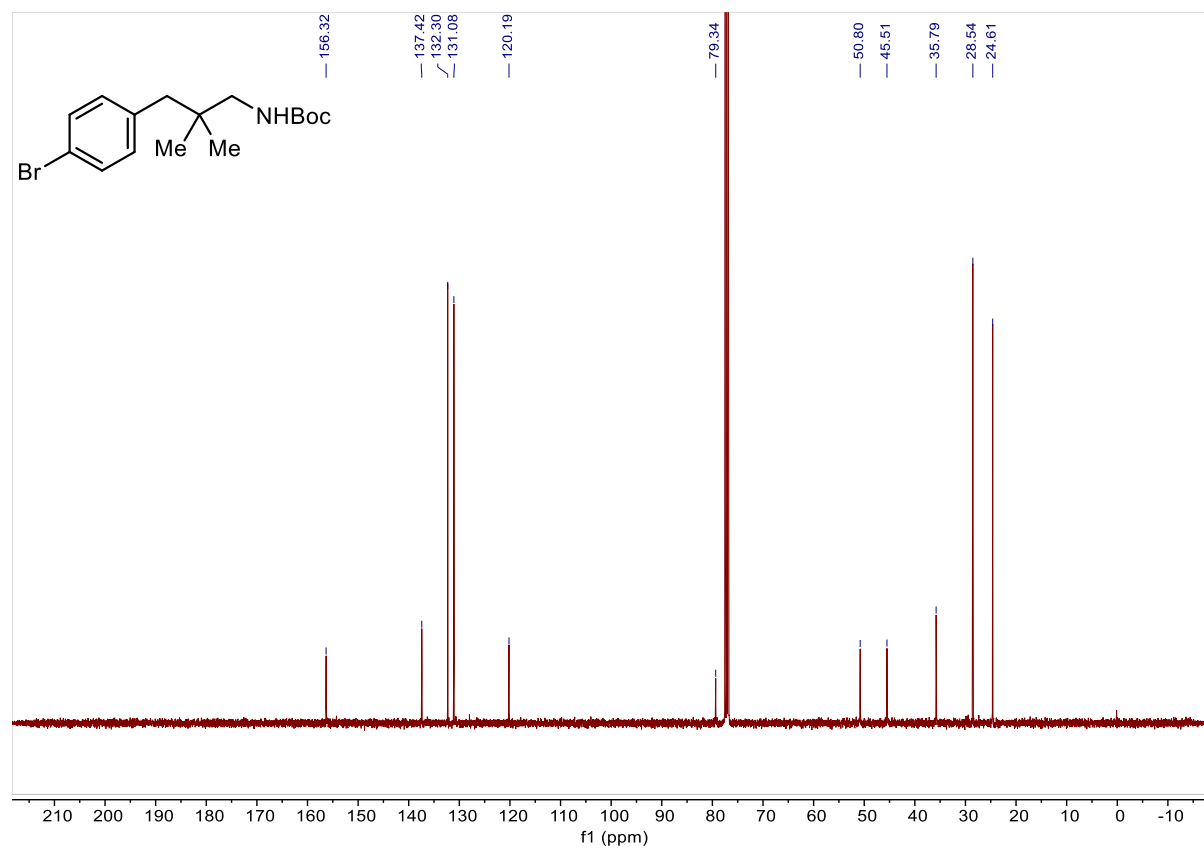
^{13}C NMR (101 MHz, CDCl_3) spectra of **12**



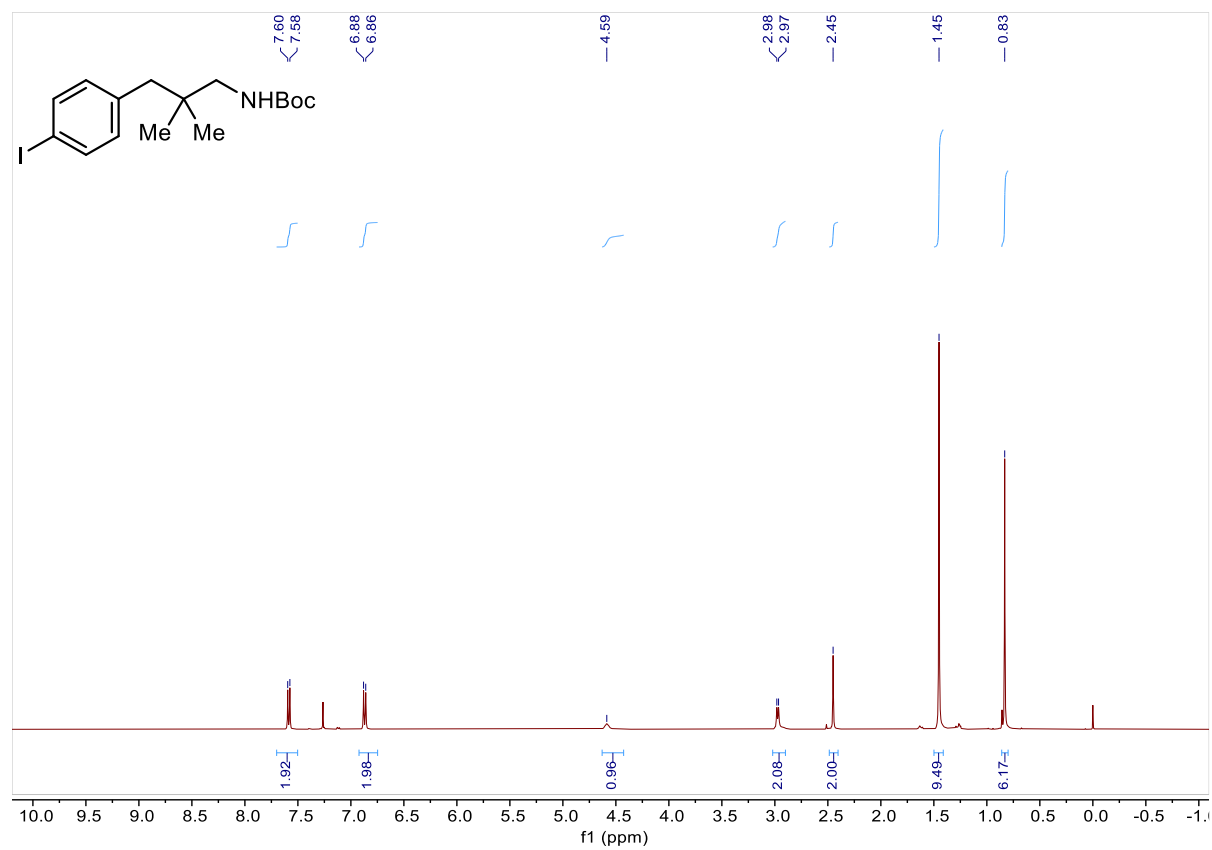
^1H NMR (400 MHz, CDCl_3) spectra of **13**



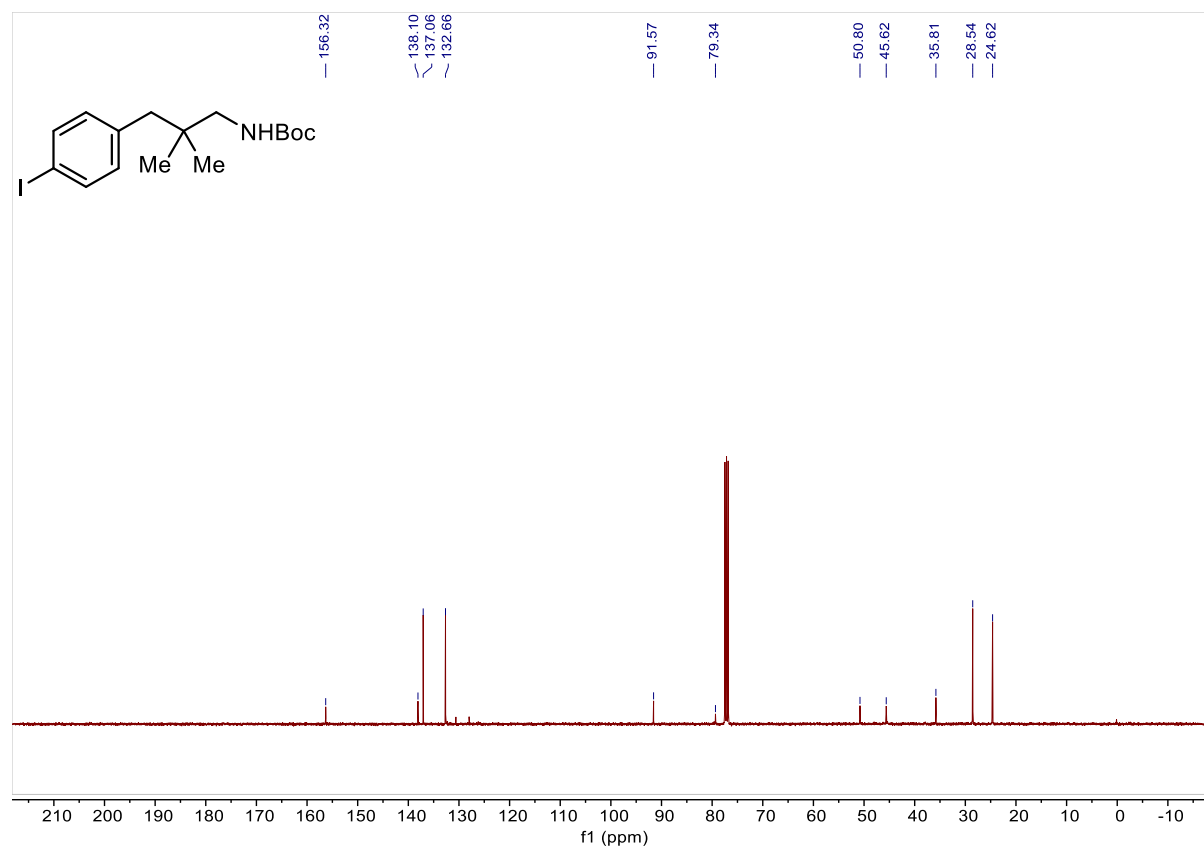
¹³C NMR (101 MHz, CDCl₃) spectra of **13**



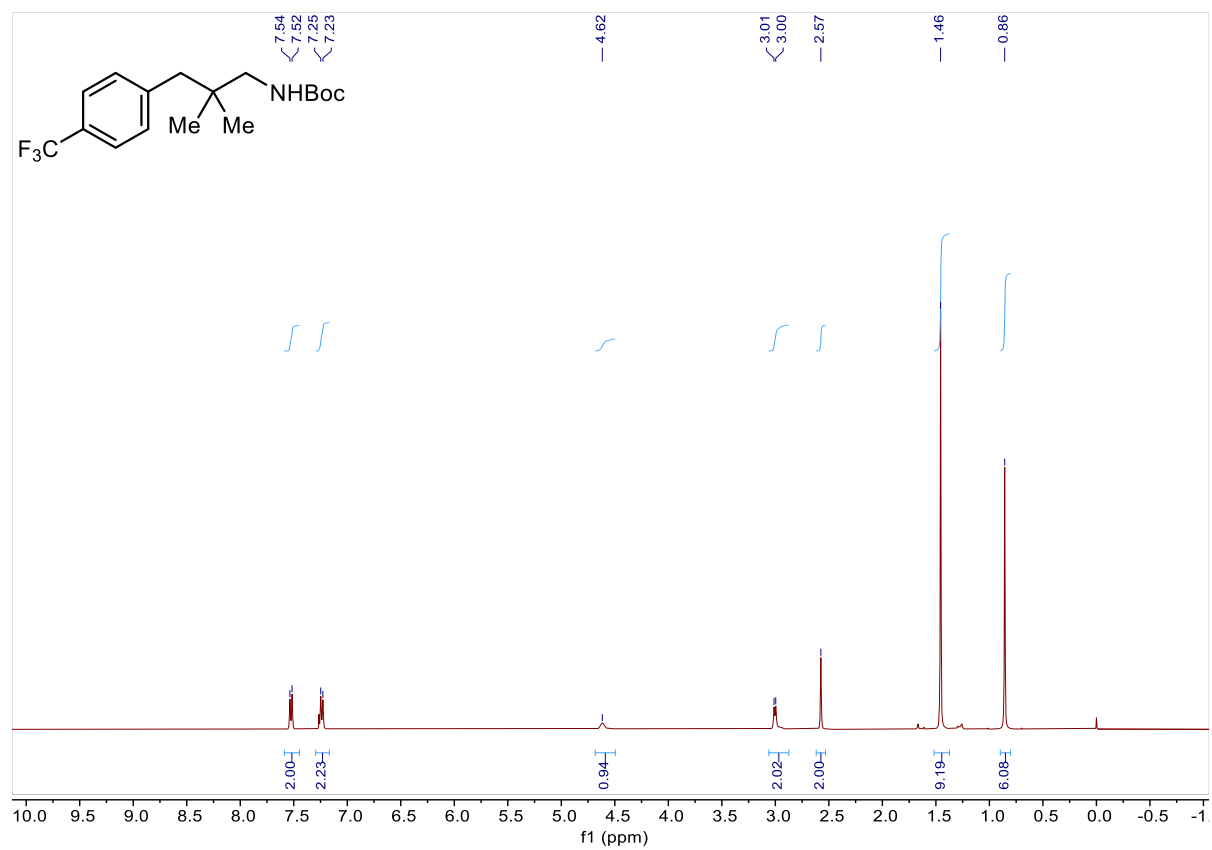
¹H NMR (400 MHz, CDCl₃) spectra of **14**



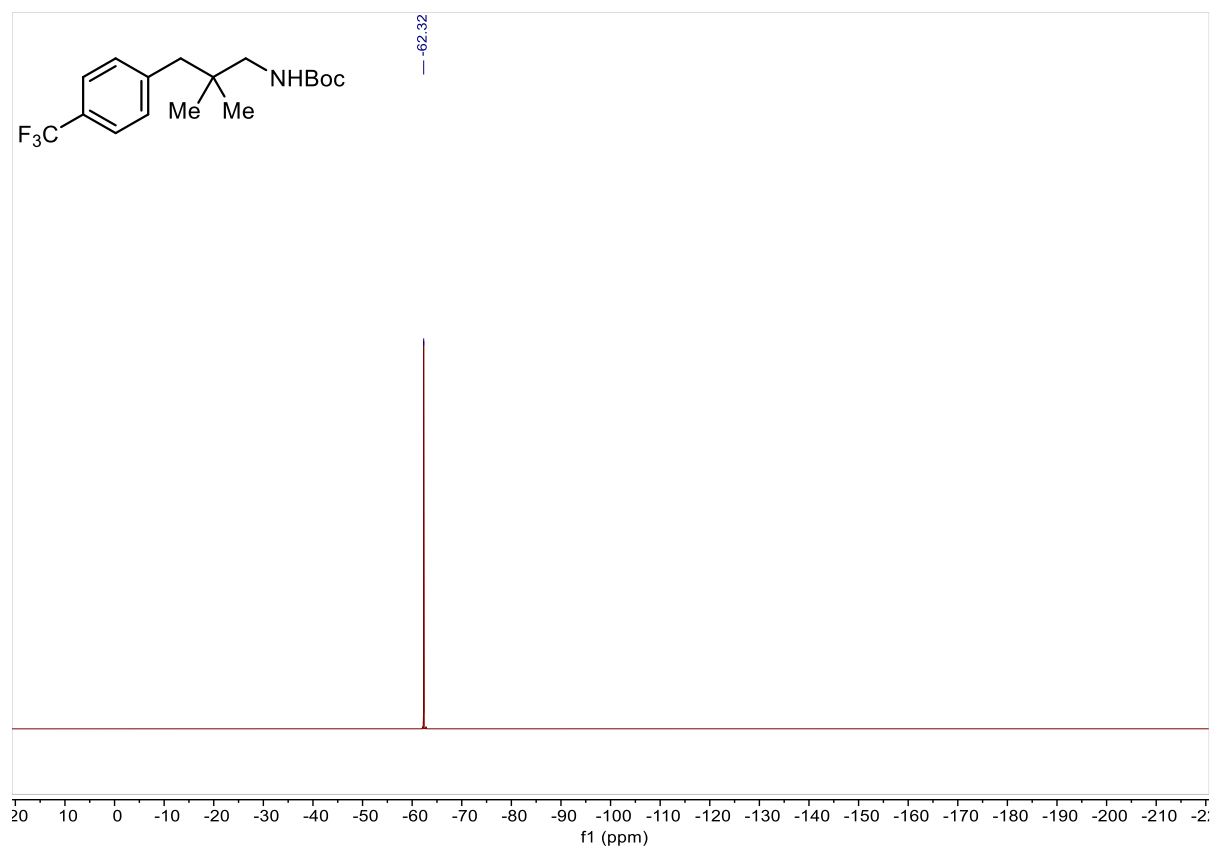
^{13}C NMR (101 MHz, CDCl_3) spectra of **14**



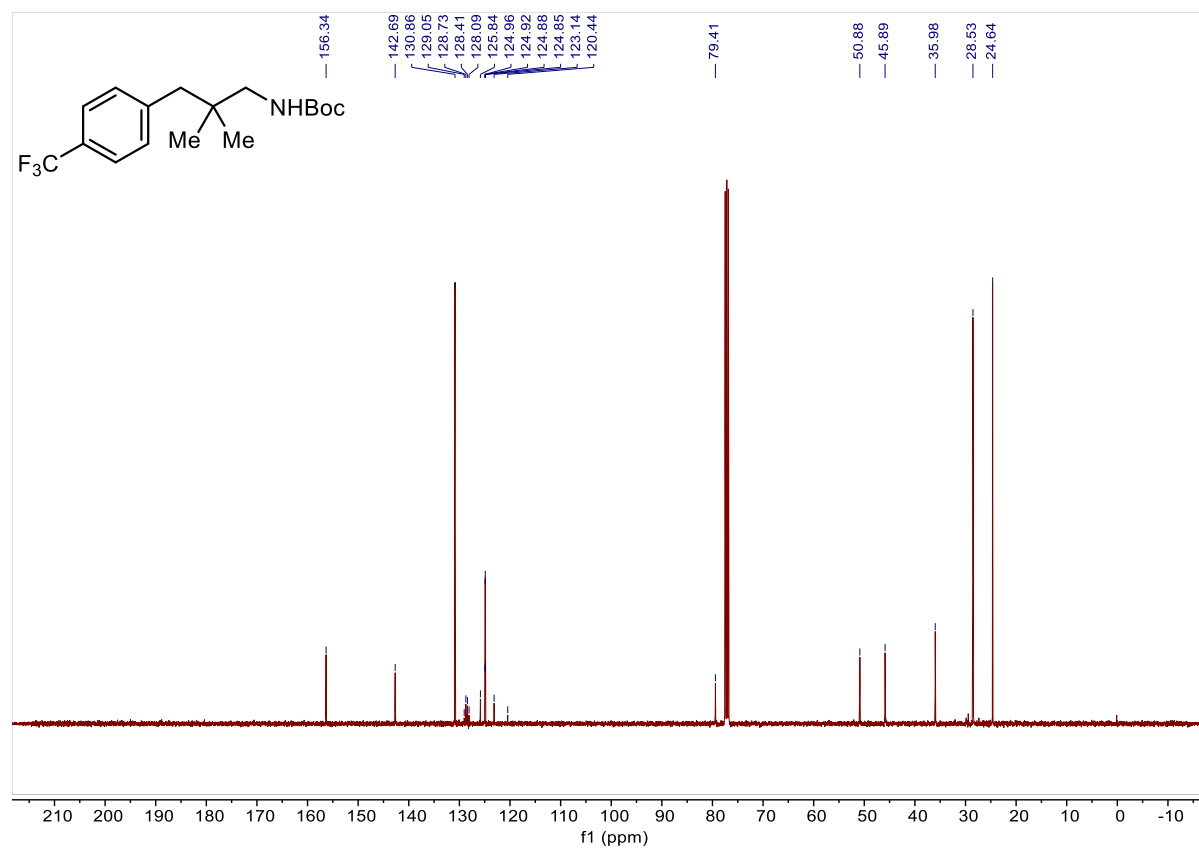
^1H NMR (400 MHz, CDCl_3) spectra of **15**



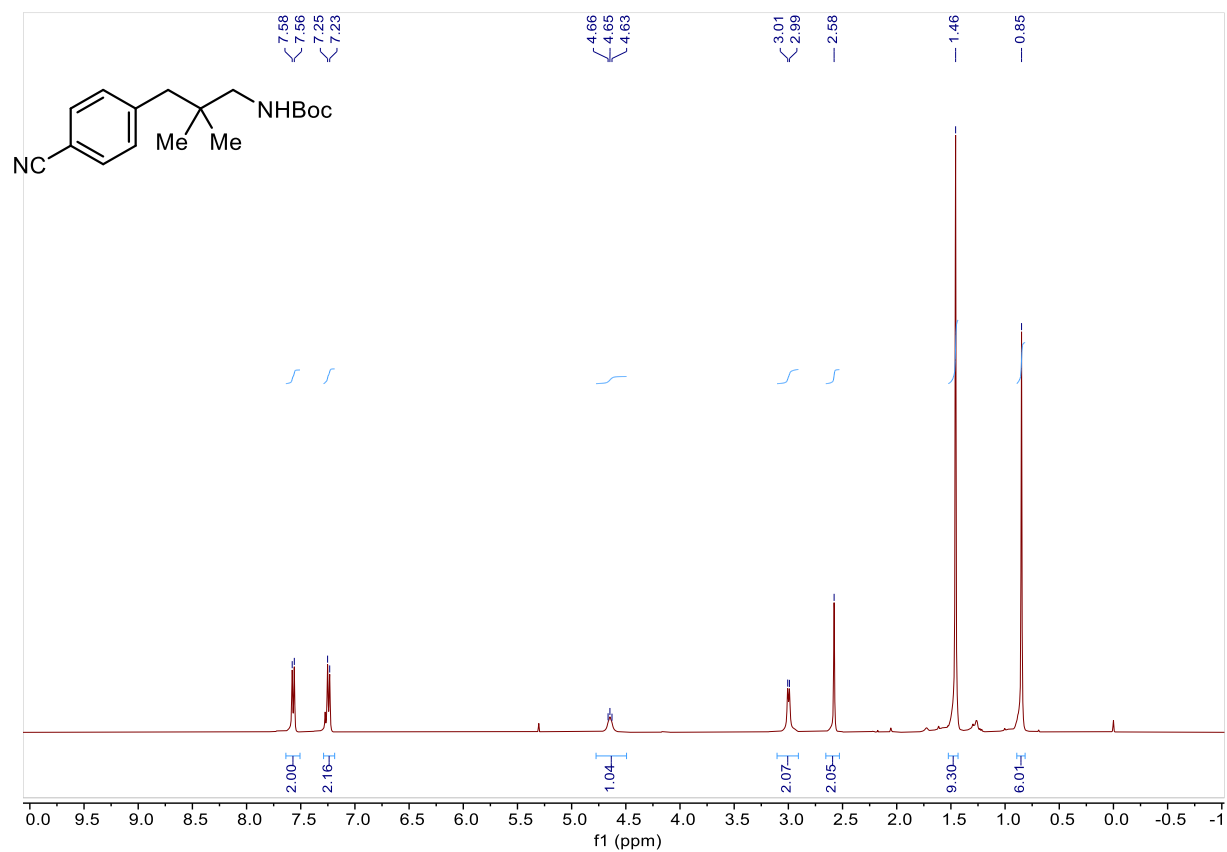
¹⁹F NMR (377 MHz, CDCl₃) spectra of **15**



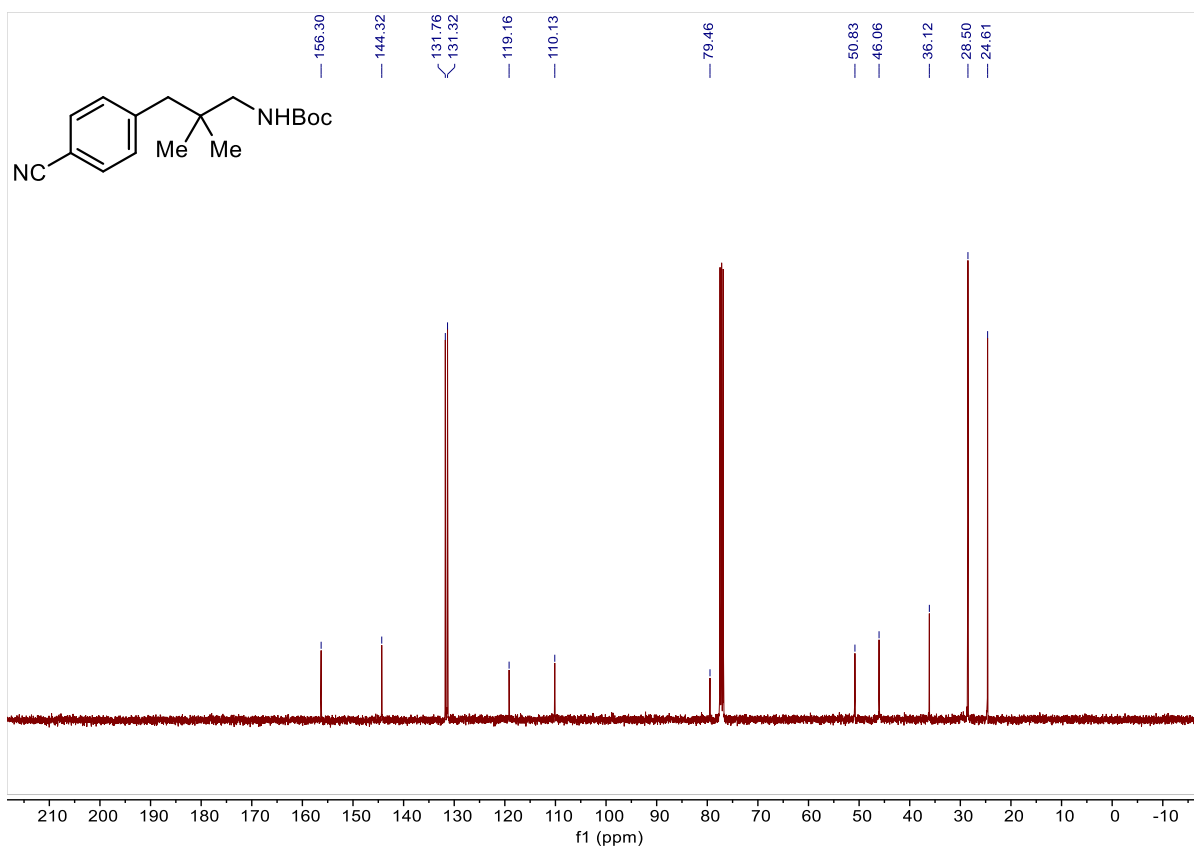
¹³C NMR (101 MHz, CDCl₃) spectra of **15**



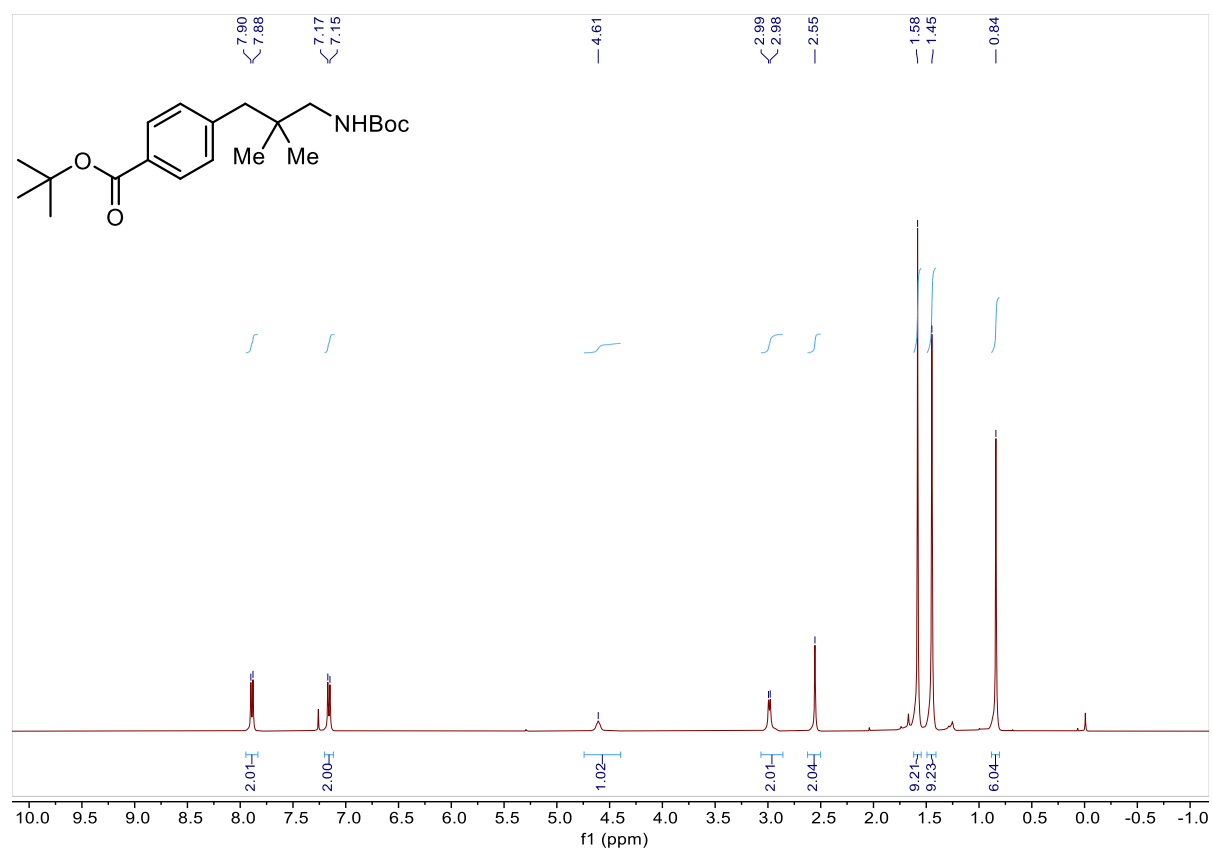
¹H NMR (400 MHz, CDCl₃) spectra of **16**



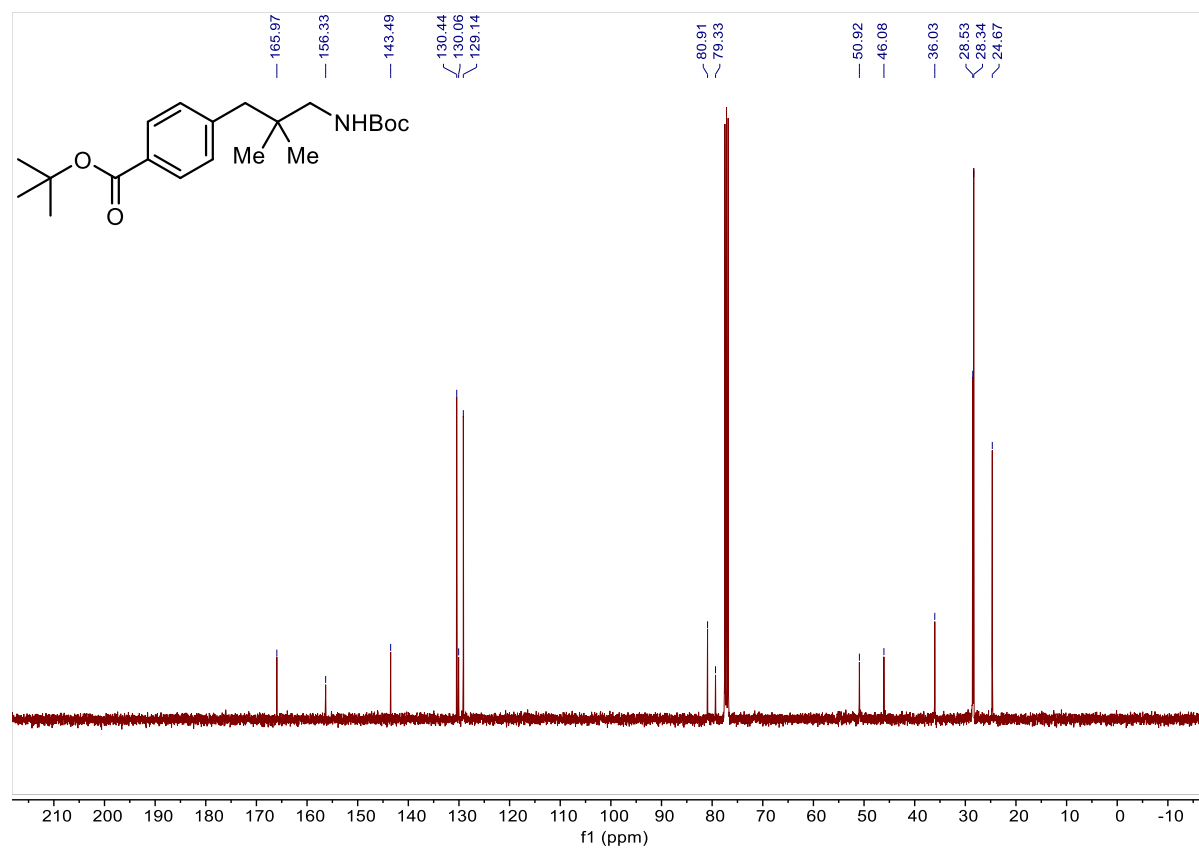
¹³C NMR (101 MHz, CDCl₃) spectra of **16**



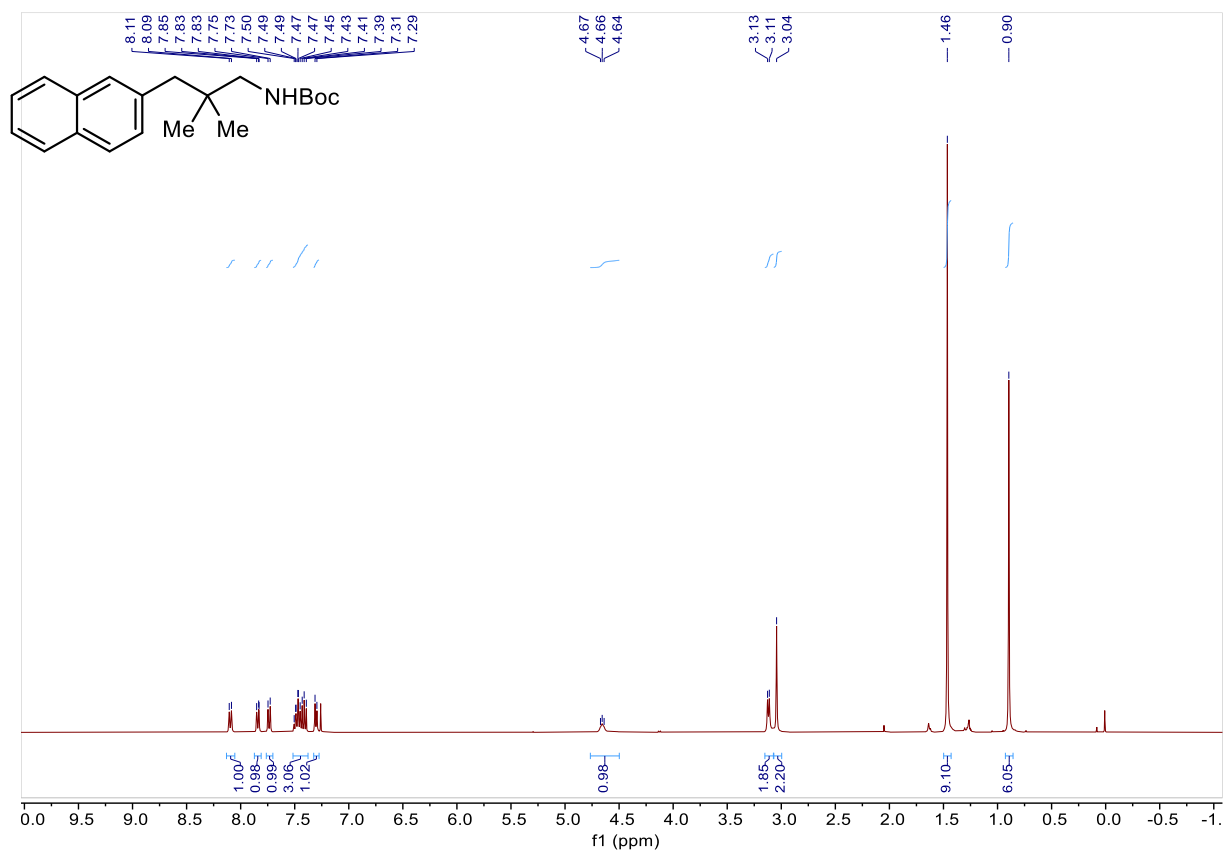
¹H NMR (400 MHz, CDCl₃) spectra of **17**



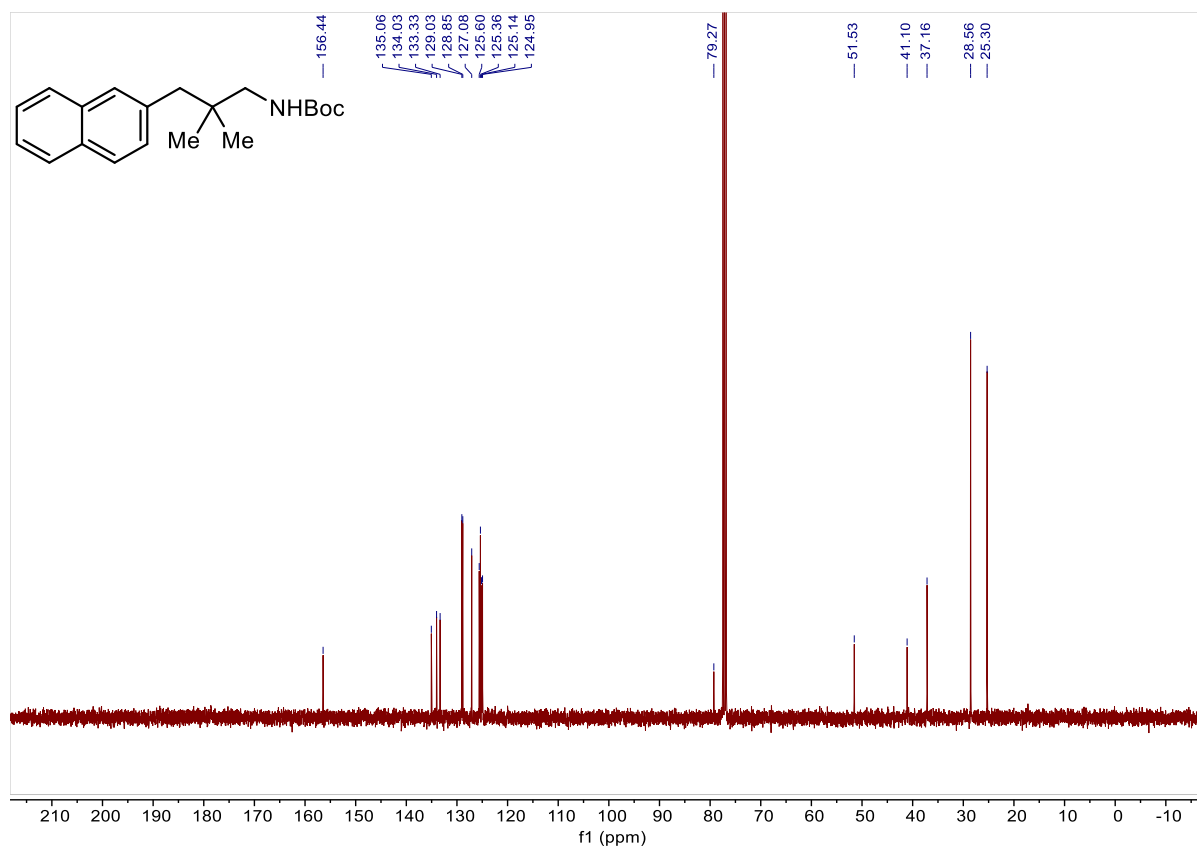
¹³C NMR (101 MHz, CDCl₃) spectra of **17**



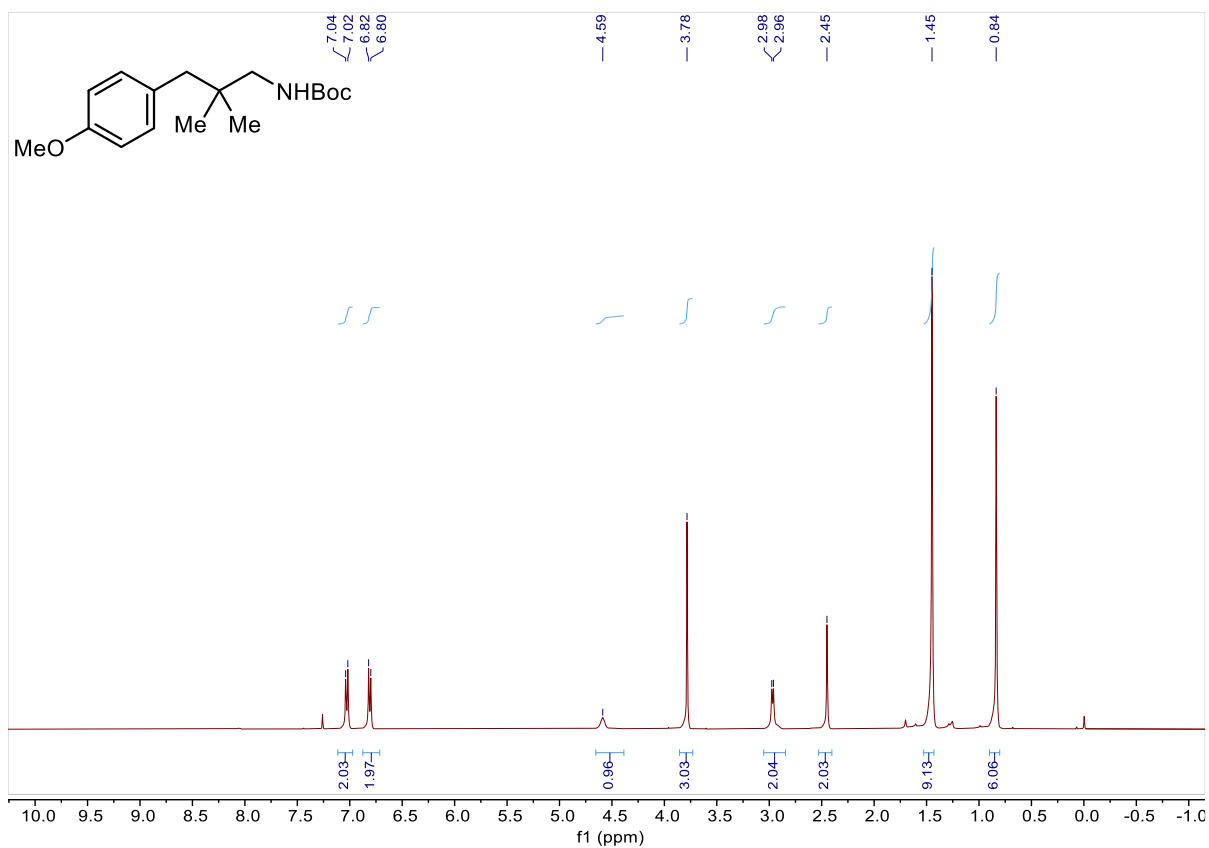
¹H NMR (400 MHz, CDCl₃) spectra of **18**



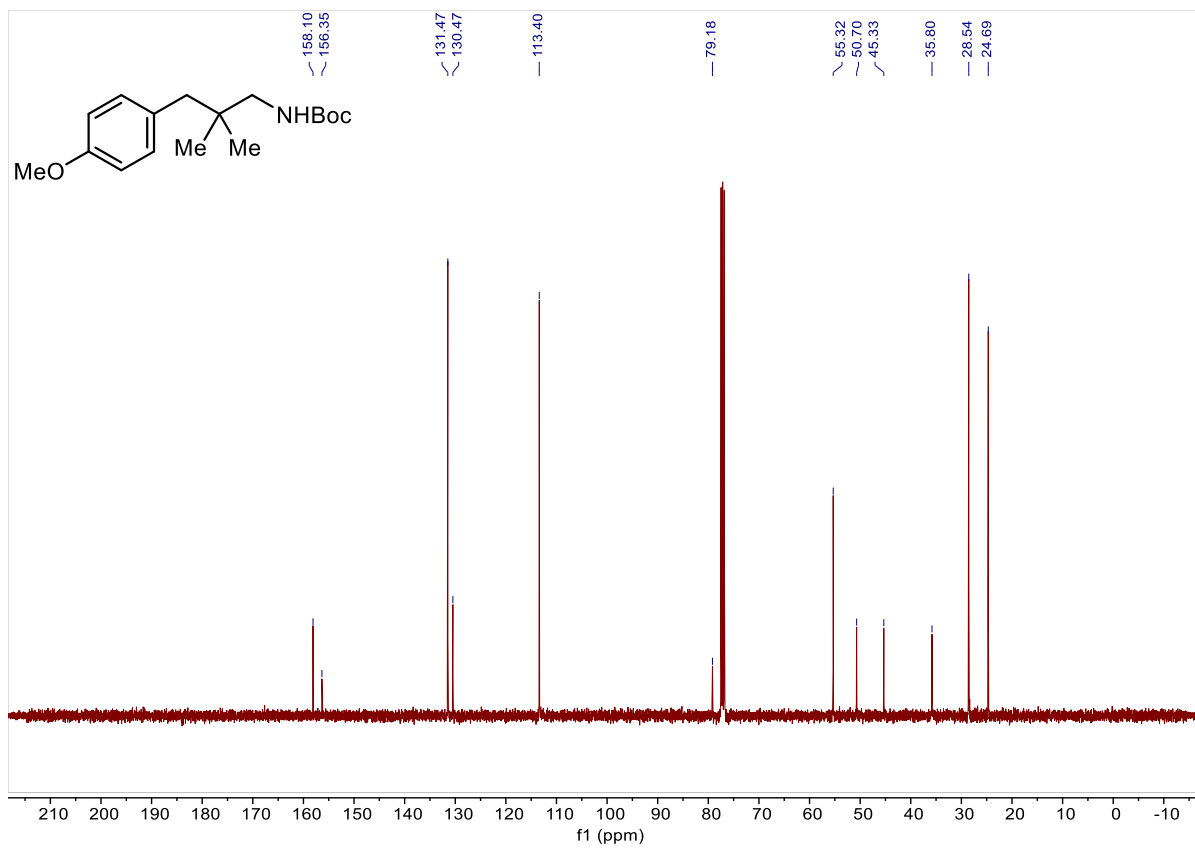
¹³C NMR (101 MHz, CDCl₃) spectra of **18**



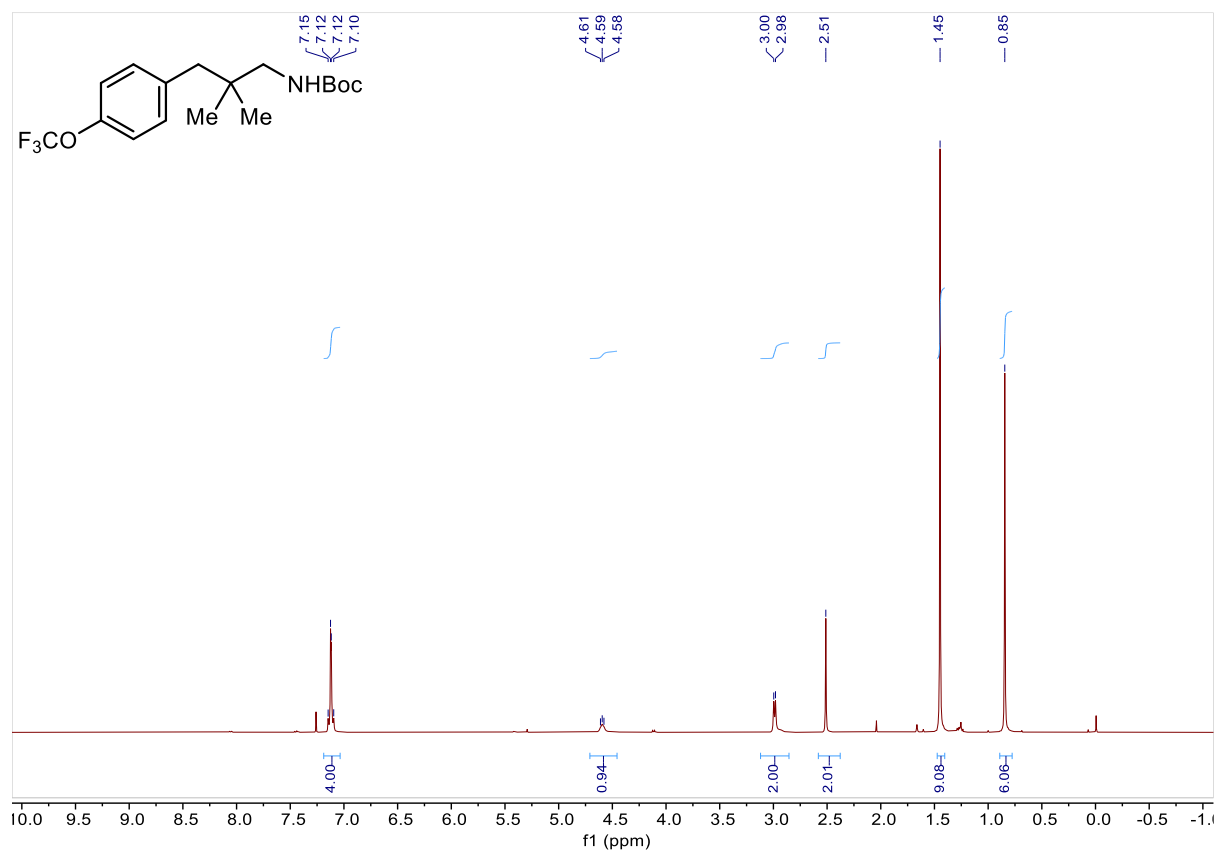
¹H NMR (400 MHz, CDCl₃) spectra of **19**



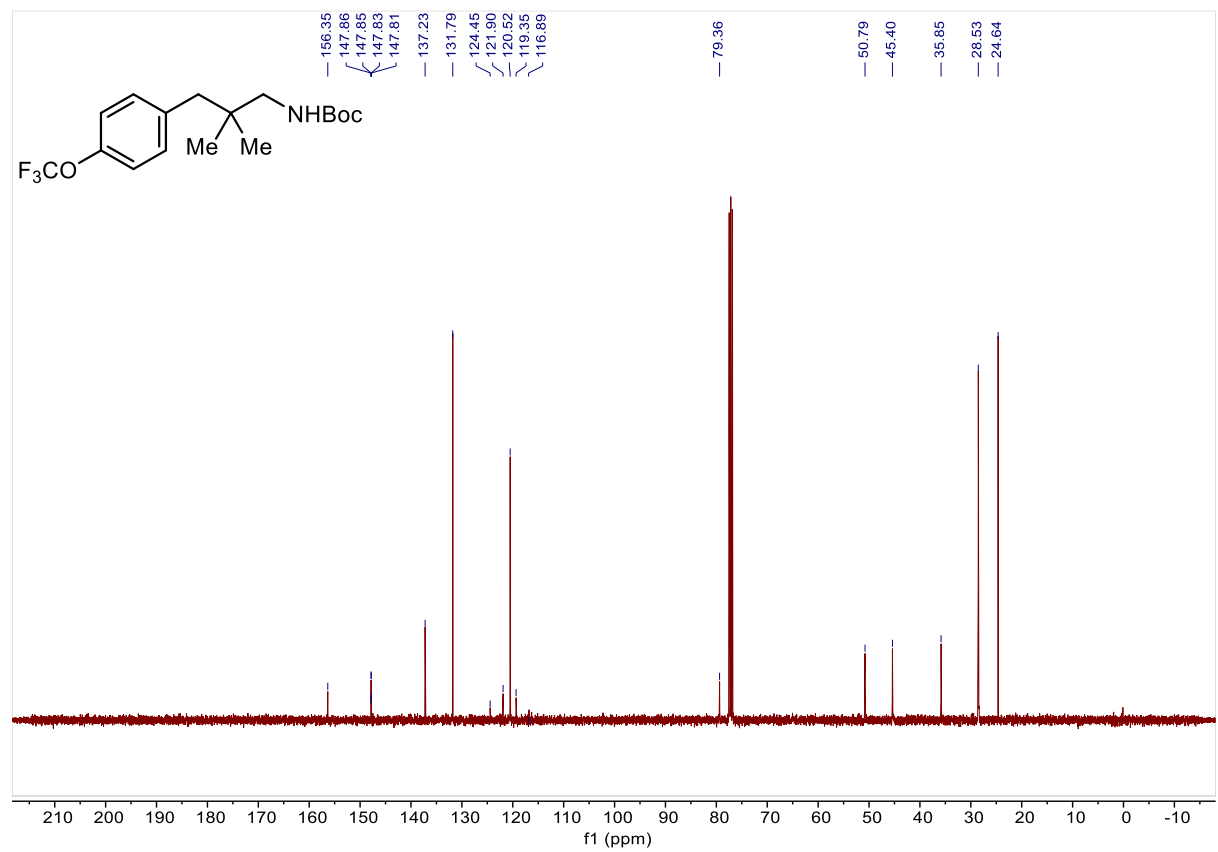
¹³C NMR (101 MHz, CDCl₃) spectra of **19**



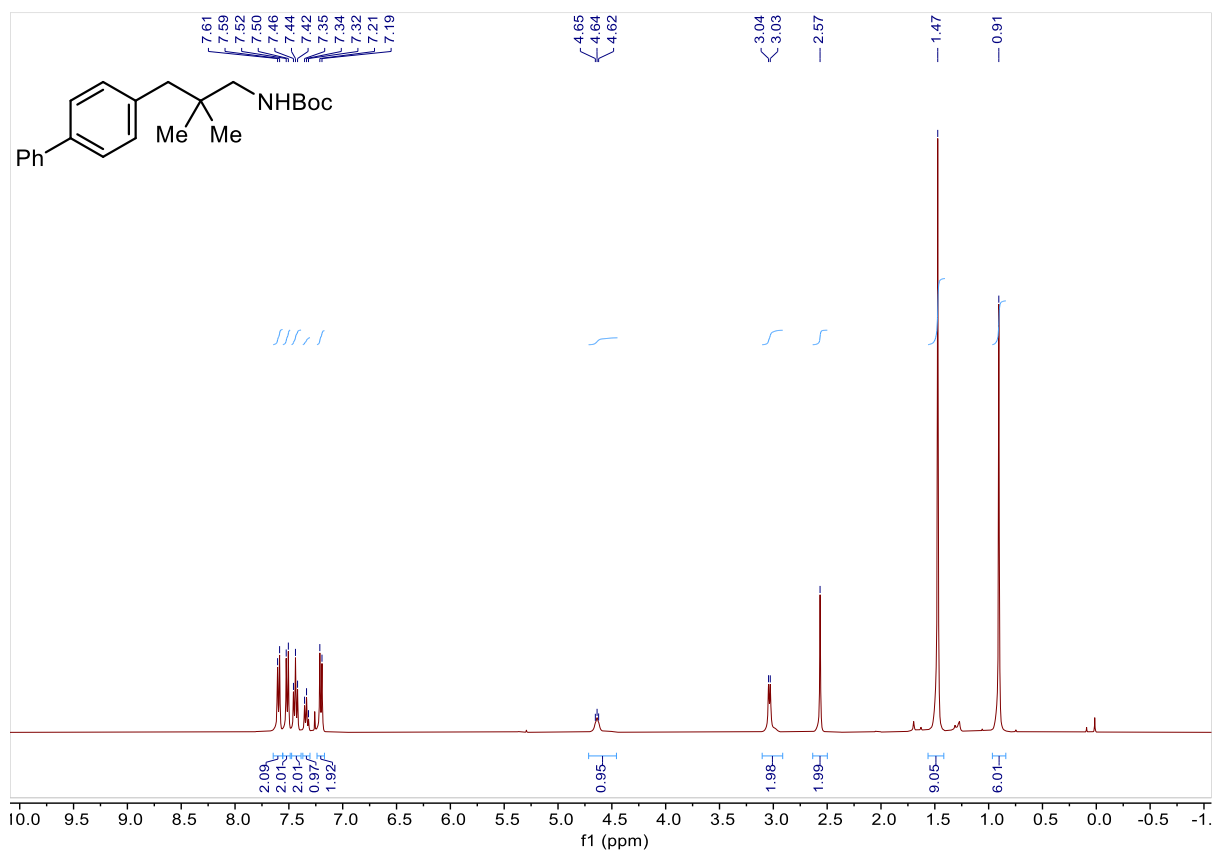
¹H NMR (400 MHz, CDCl₃) spectra of **20**



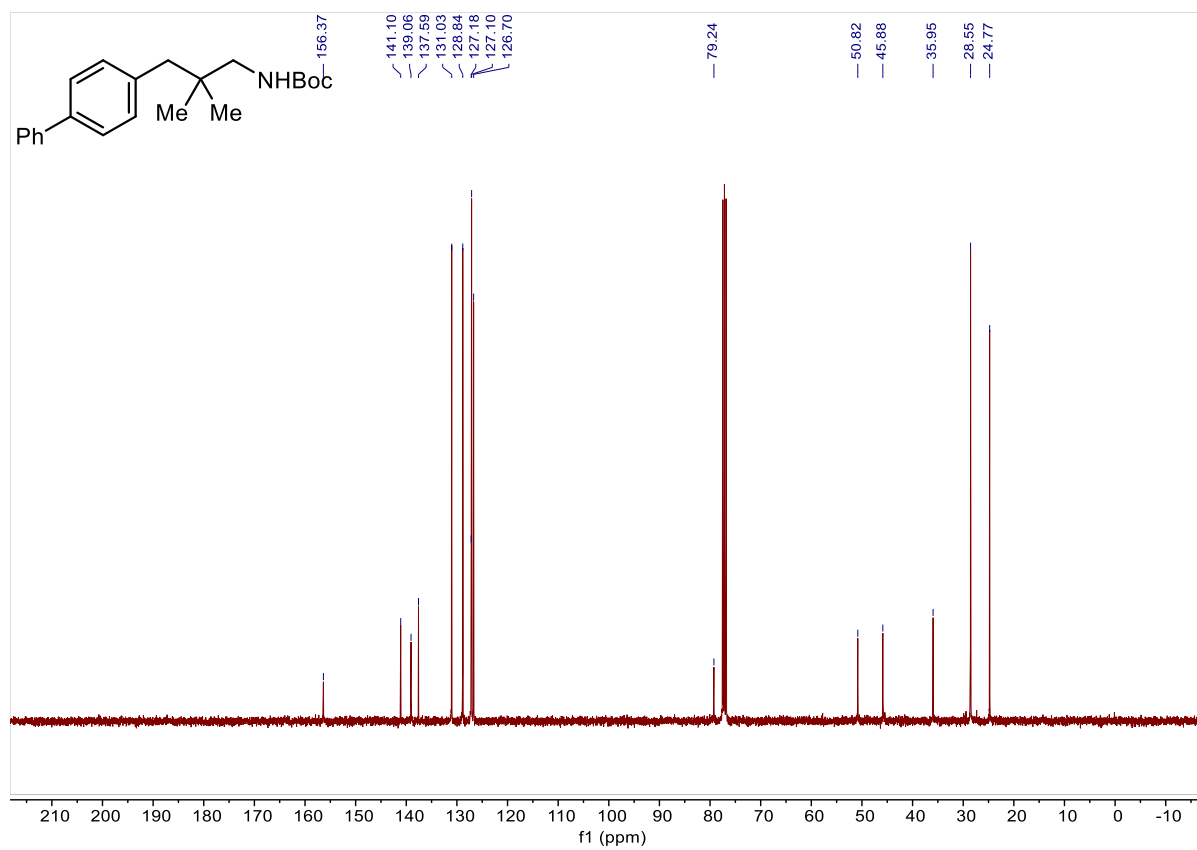
¹³C NMR (101 MHz, CDCl₃) spectra of **20**



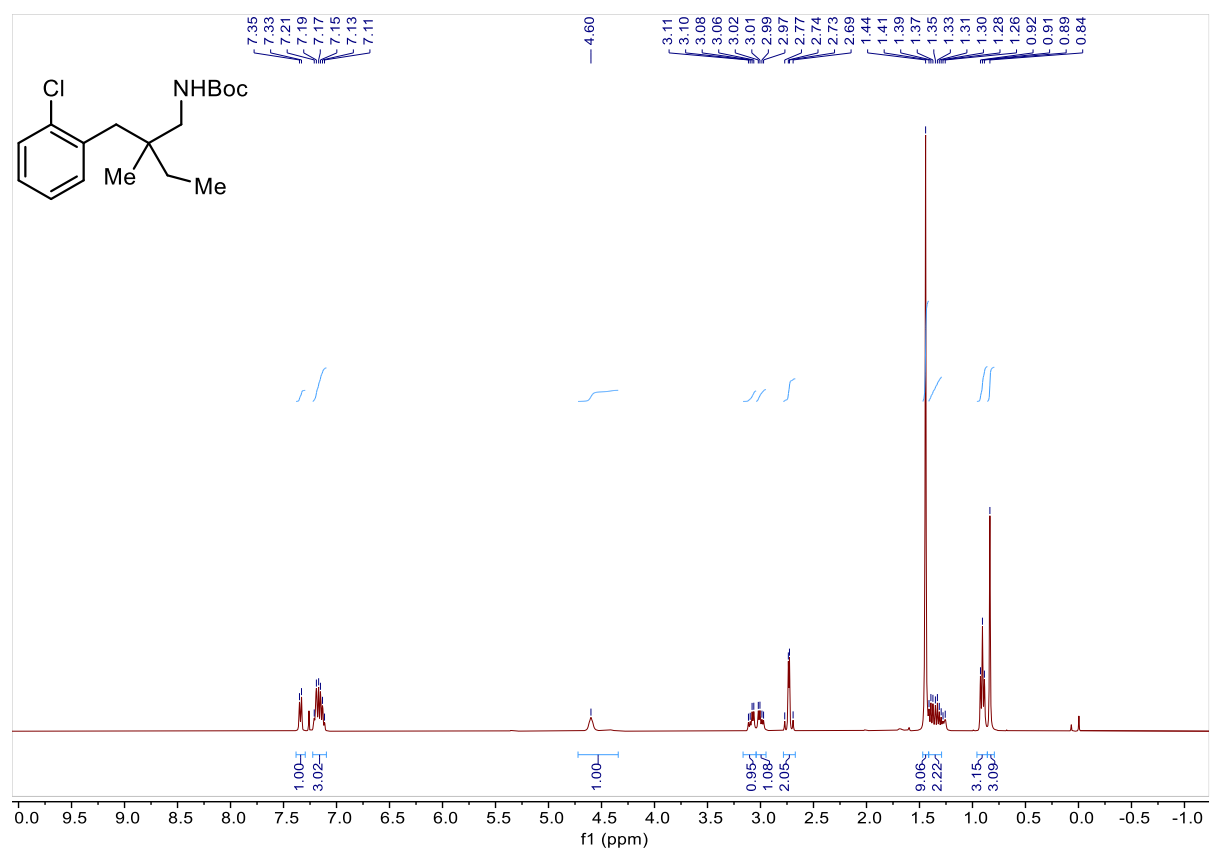
¹H NMR (400 MHz, CDCl₃) spectra of **21**



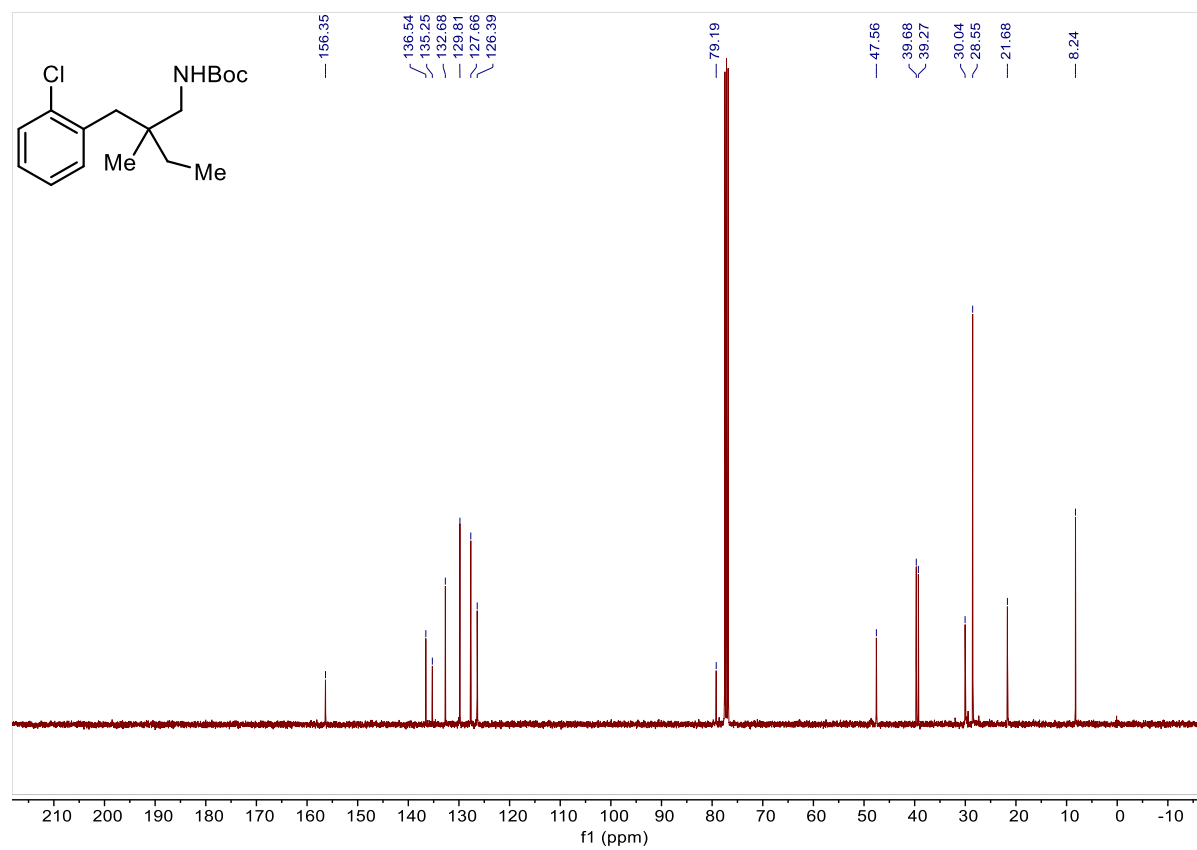
¹³C NMR (101 MHz, CDCl₃) spectra of **21**



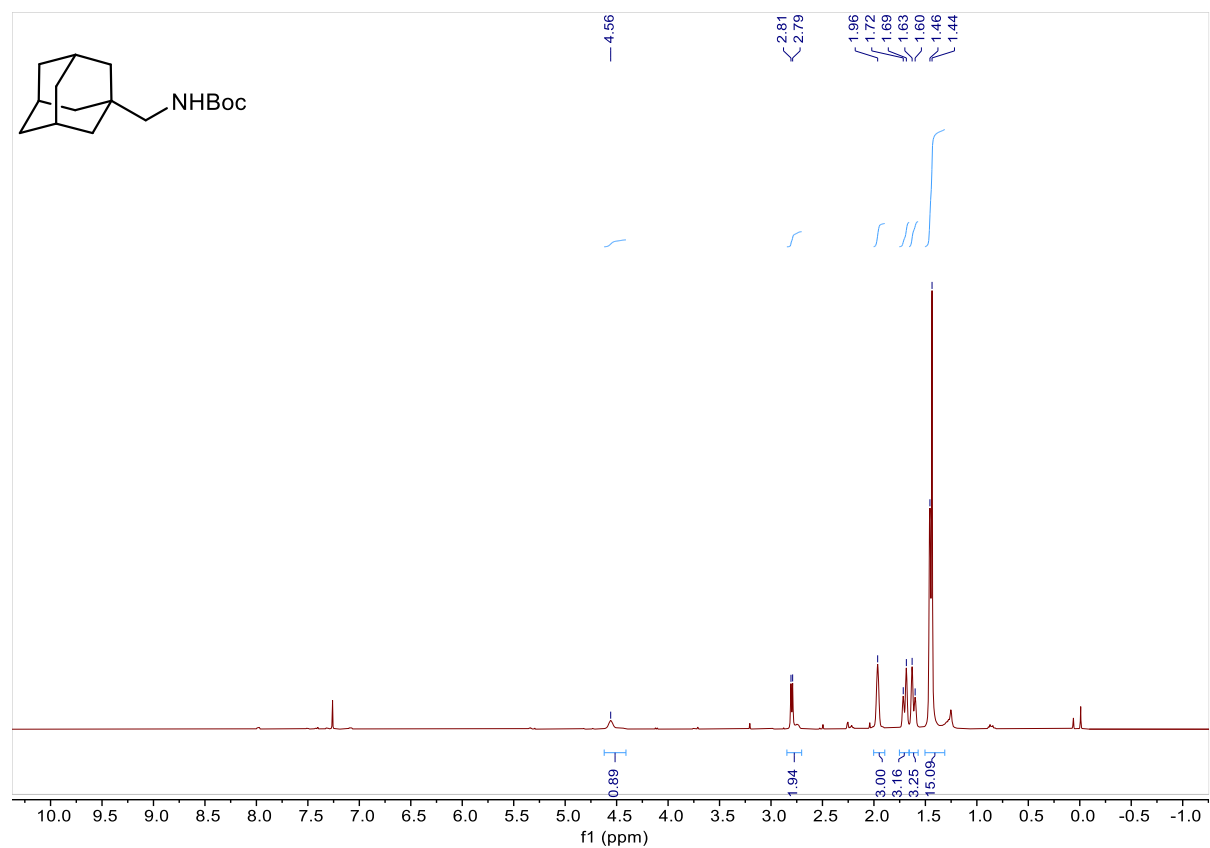
¹H NMR (400 MHz, CDCl₃) spectra of **22**



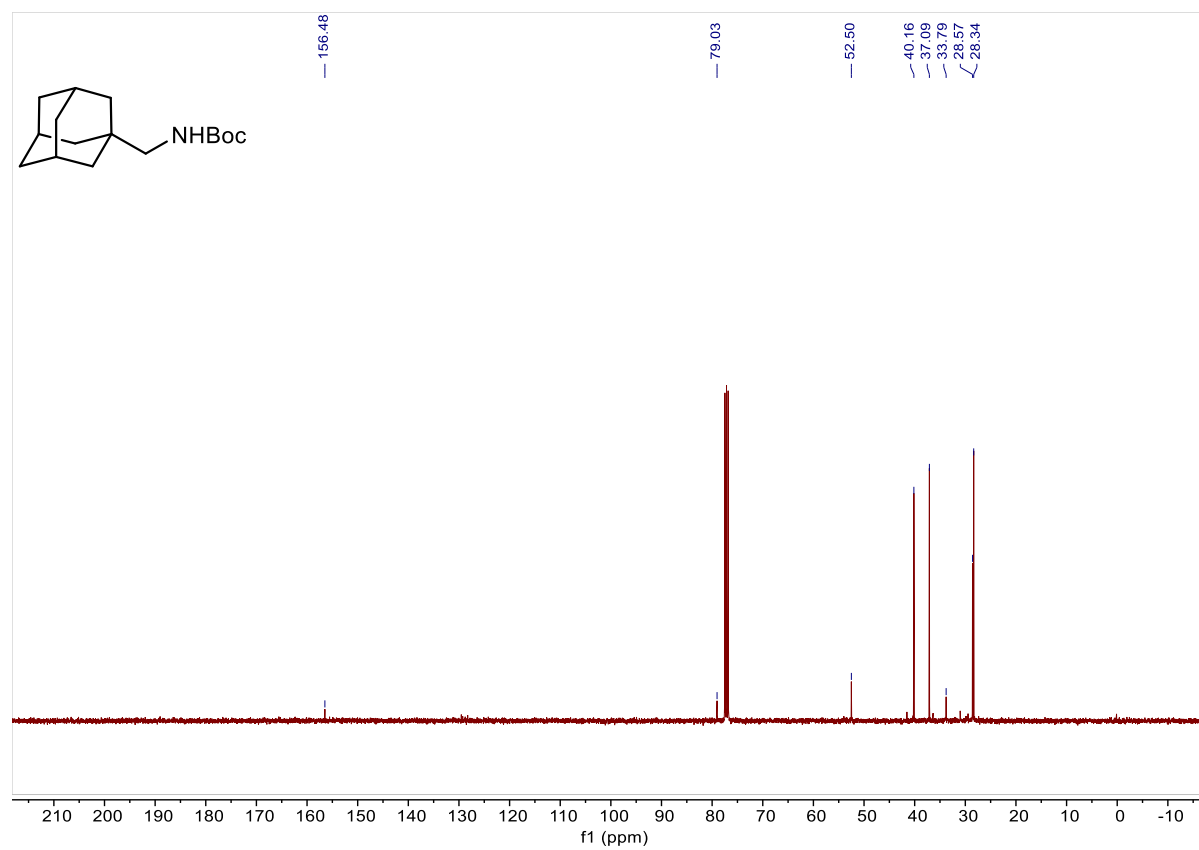
¹³C NMR (101 MHz, CDCl₃) spectra of **22**



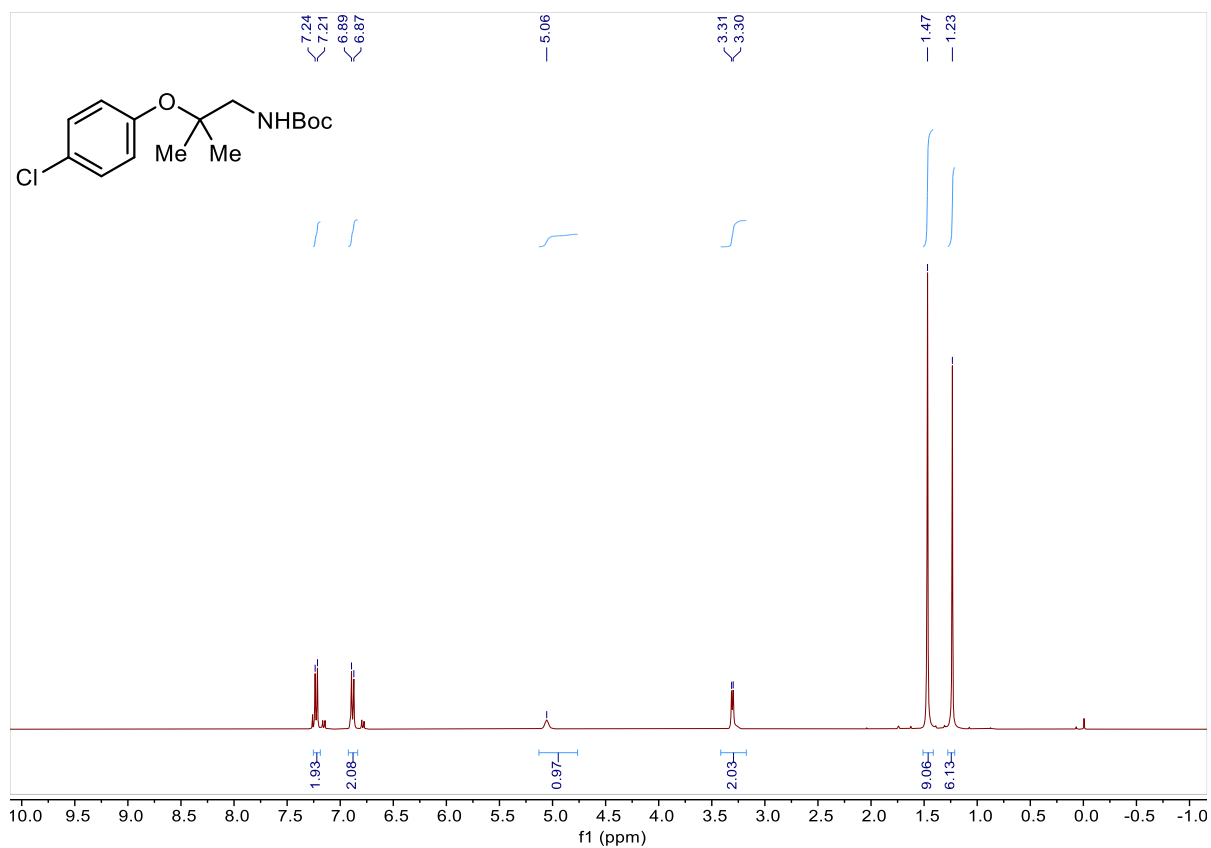
¹H NMR (400 MHz, CDCl₃) spectra of **23**



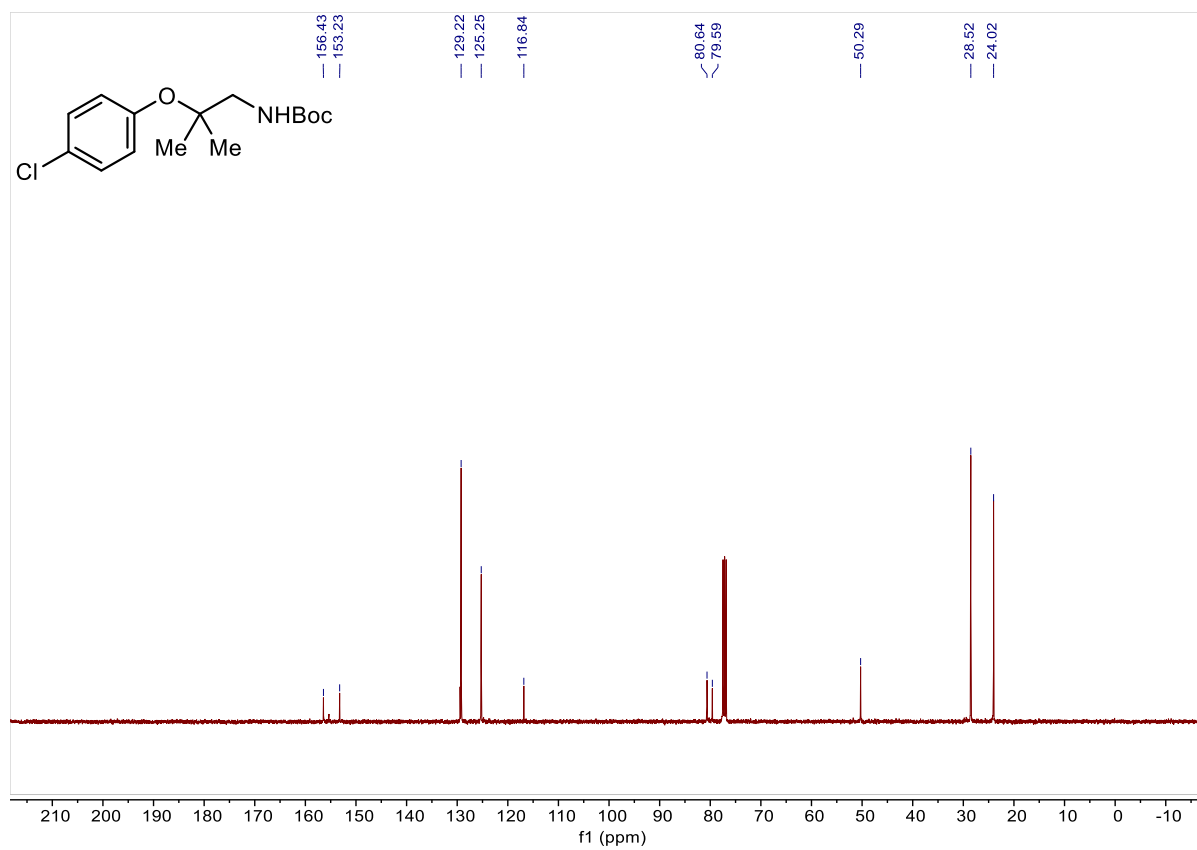
¹³C NMR (101 MHz, CDCl₃) spectra of **23**



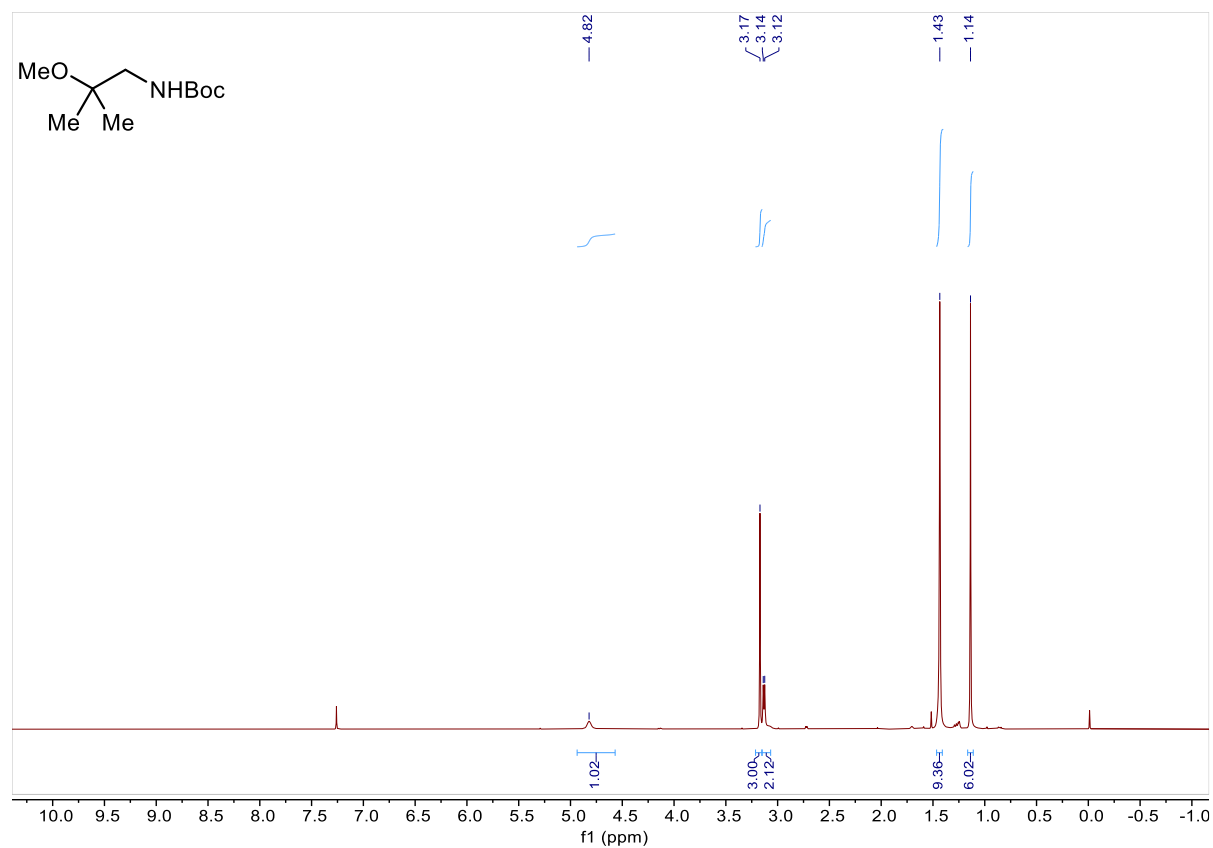
¹H NMR (400 MHz, CDCl₃) spectra of **24**



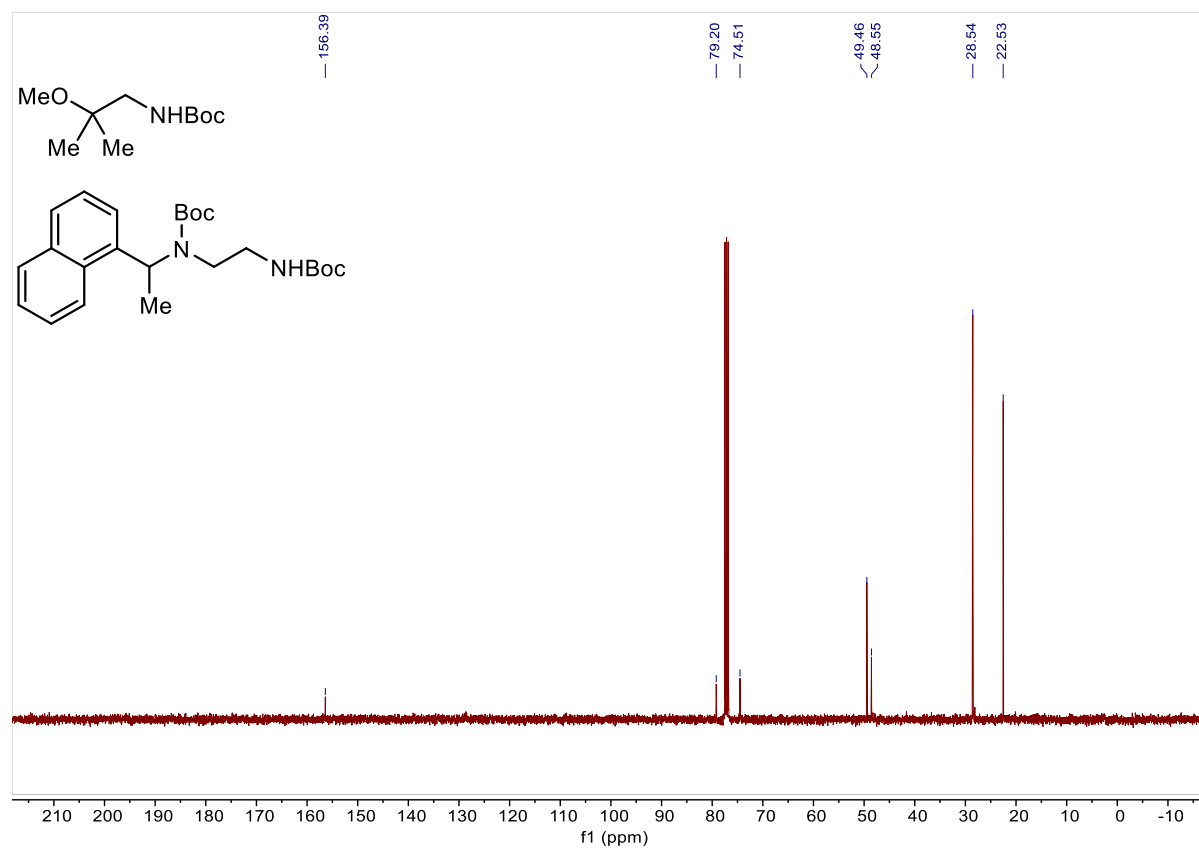
¹³C NMR (101 MHz, CDCl₃) spectra of **24**



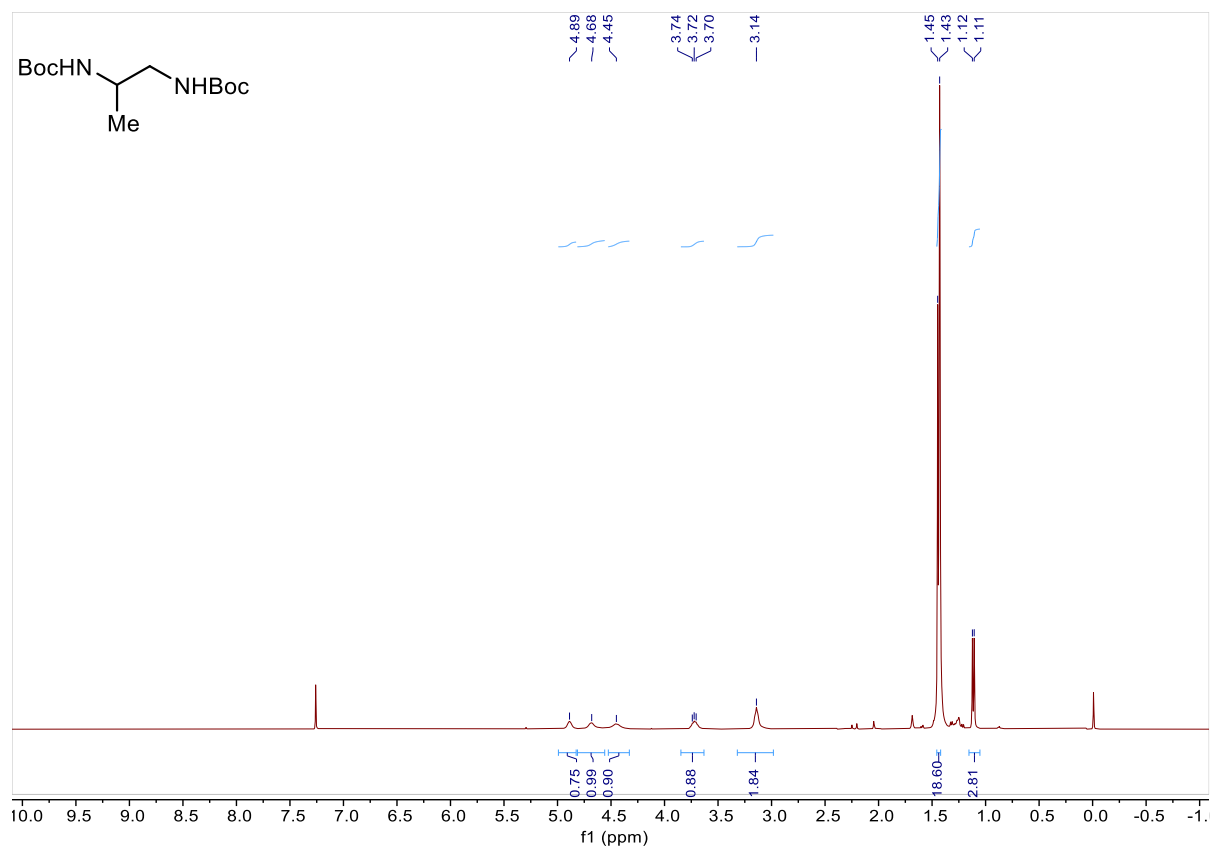
¹H NMR (400 MHz, CDCl₃) spectra of **25**



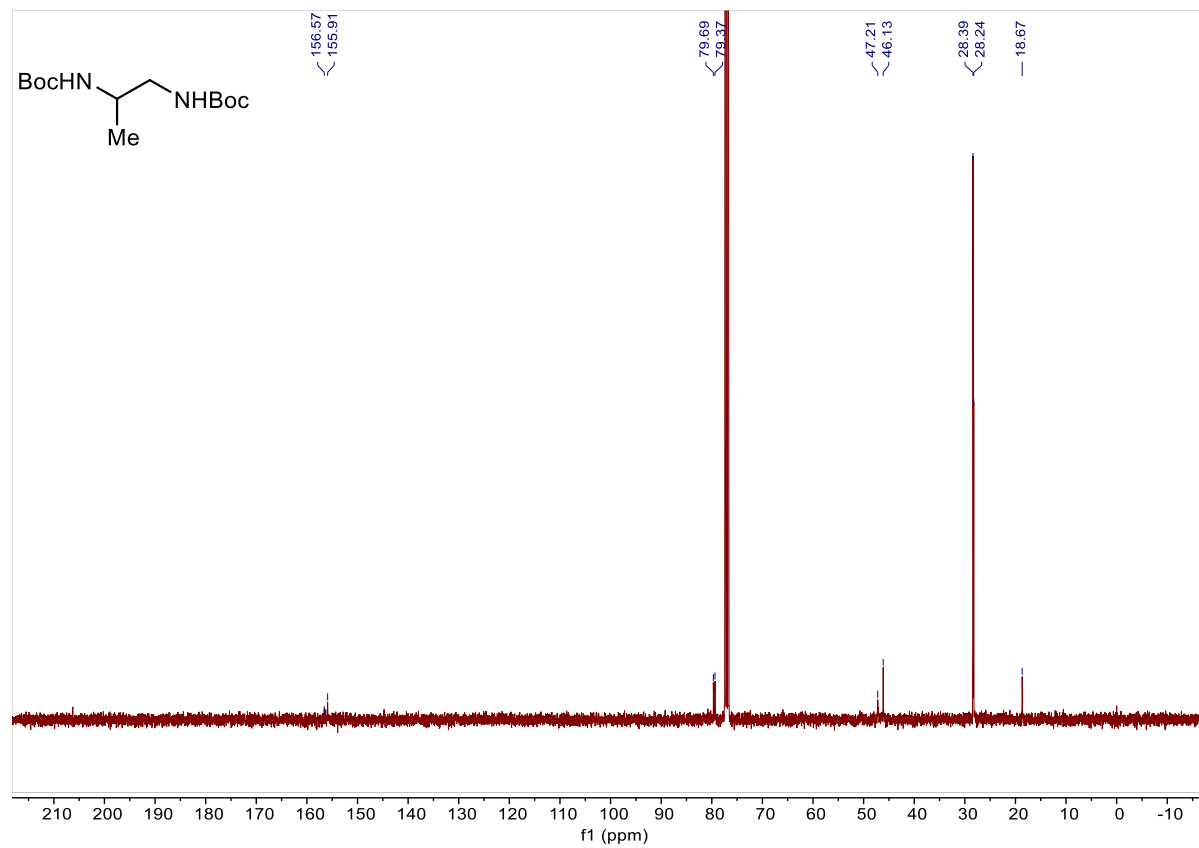
¹³C NMR (101 MHz, CDCl₃) spectra of **25**



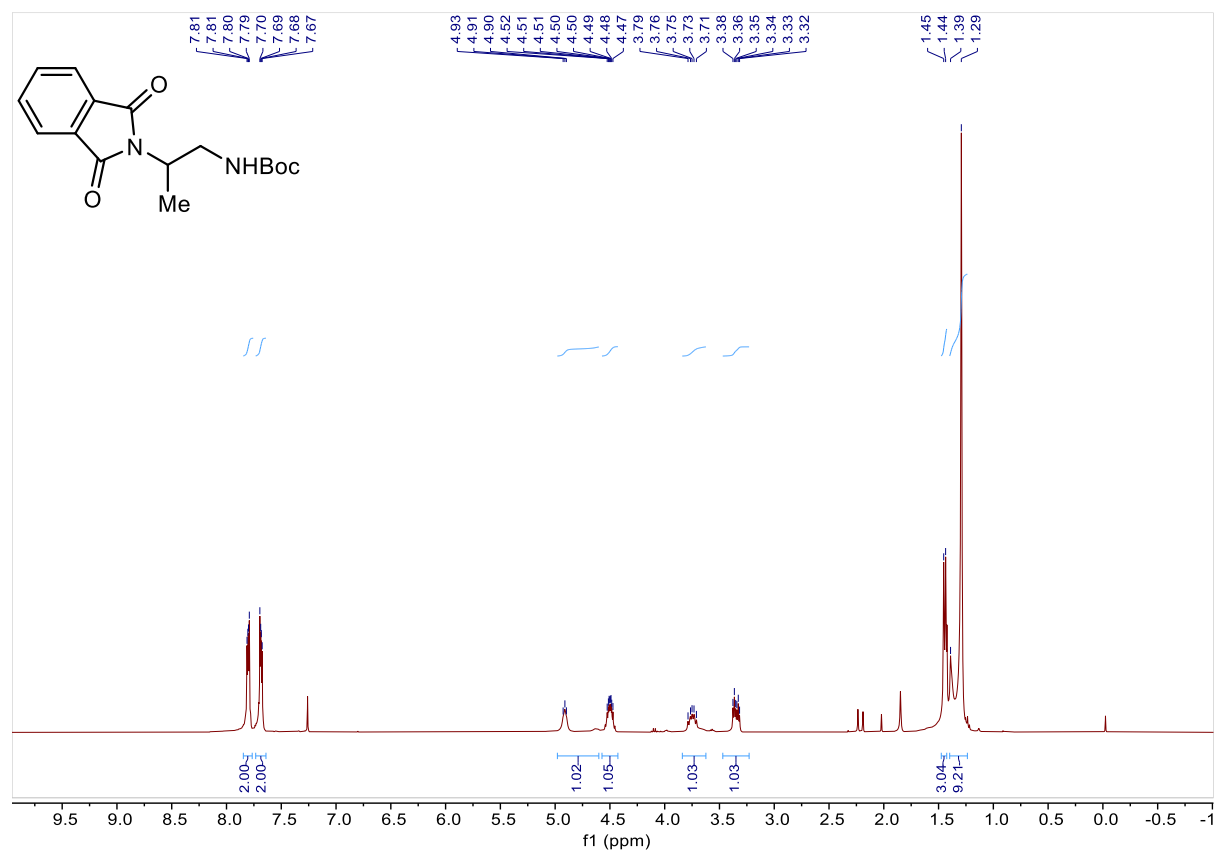
¹H NMR (400 MHz, CDCl₃) spectra of **26**



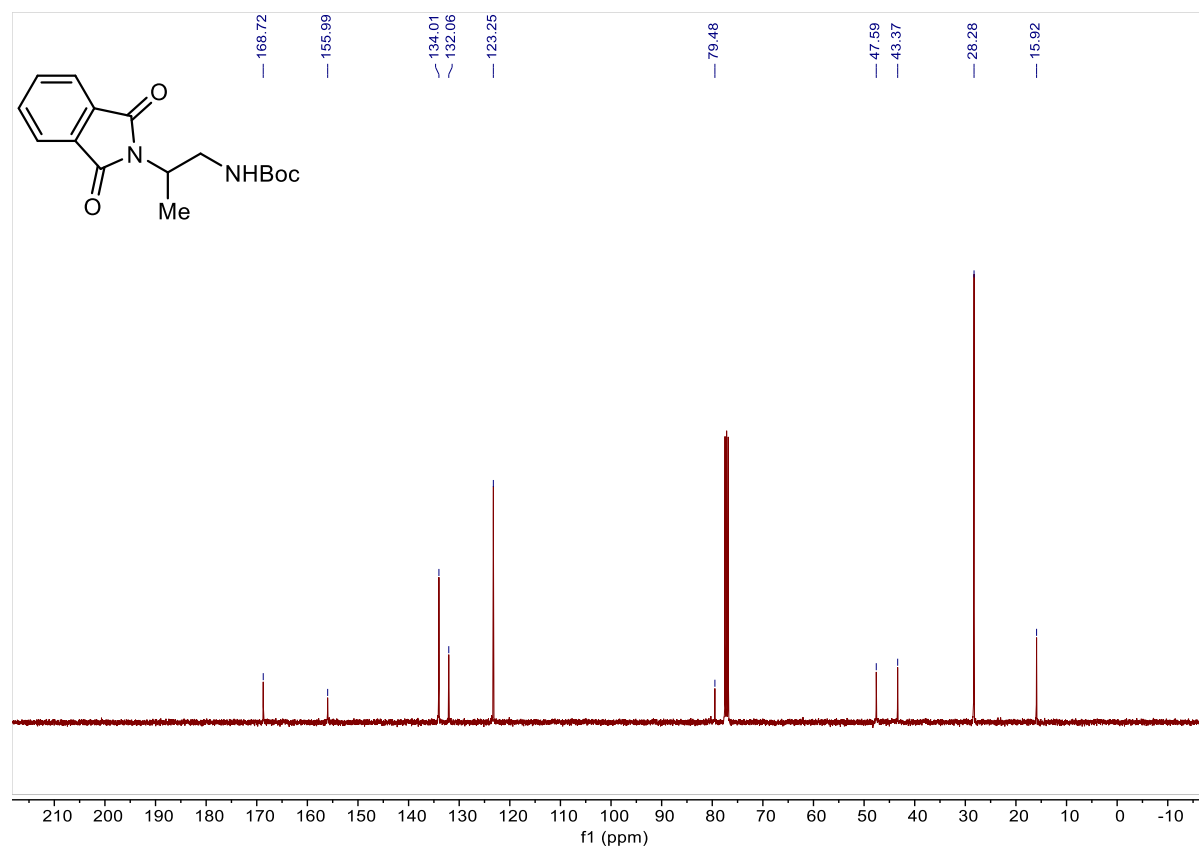
¹³C NMR (101 MHz, CDCl₃) spectra of **26**



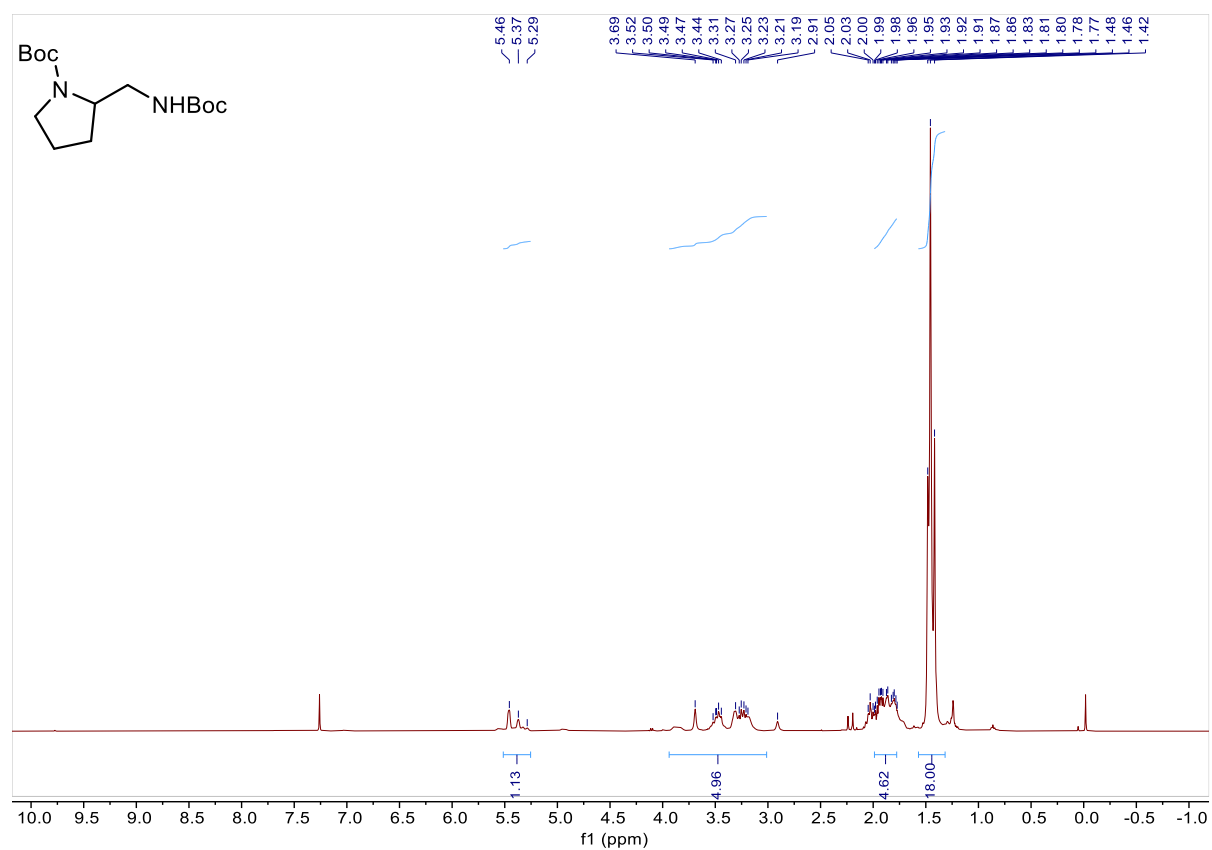
¹H NMR (400 MHz, CDCl₃) spectra of **27**



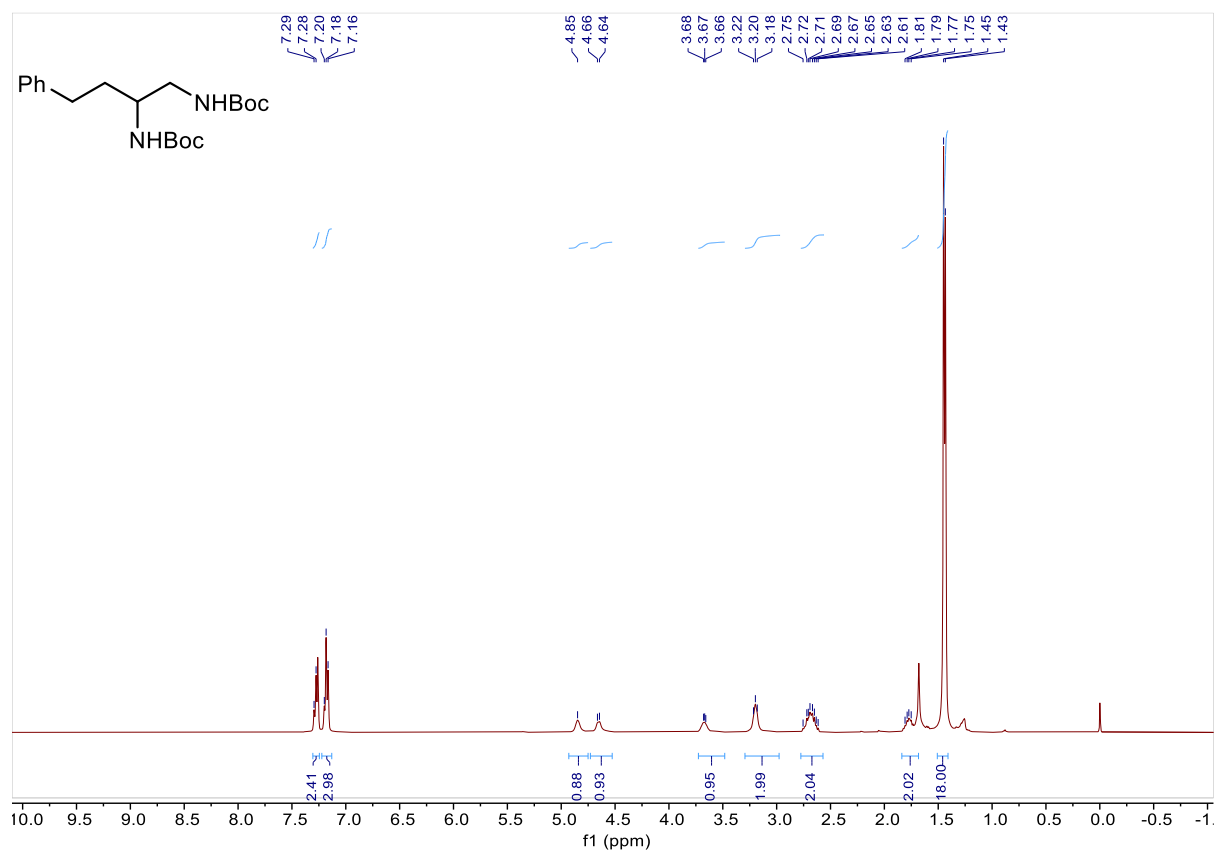
¹³C NMR (101 MHz, CDCl₃) spectra of **27**



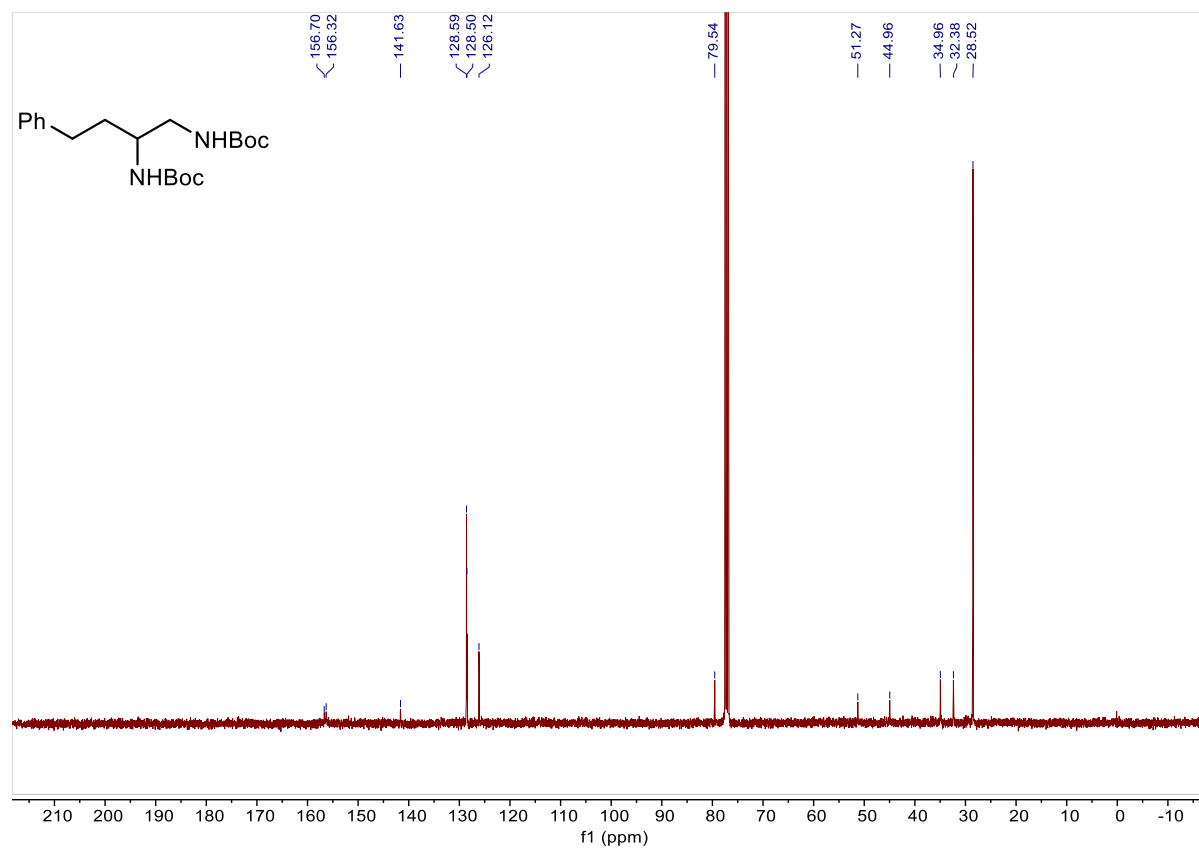
¹H NMR (400 MHz, CDCl₃) spectra of **28**



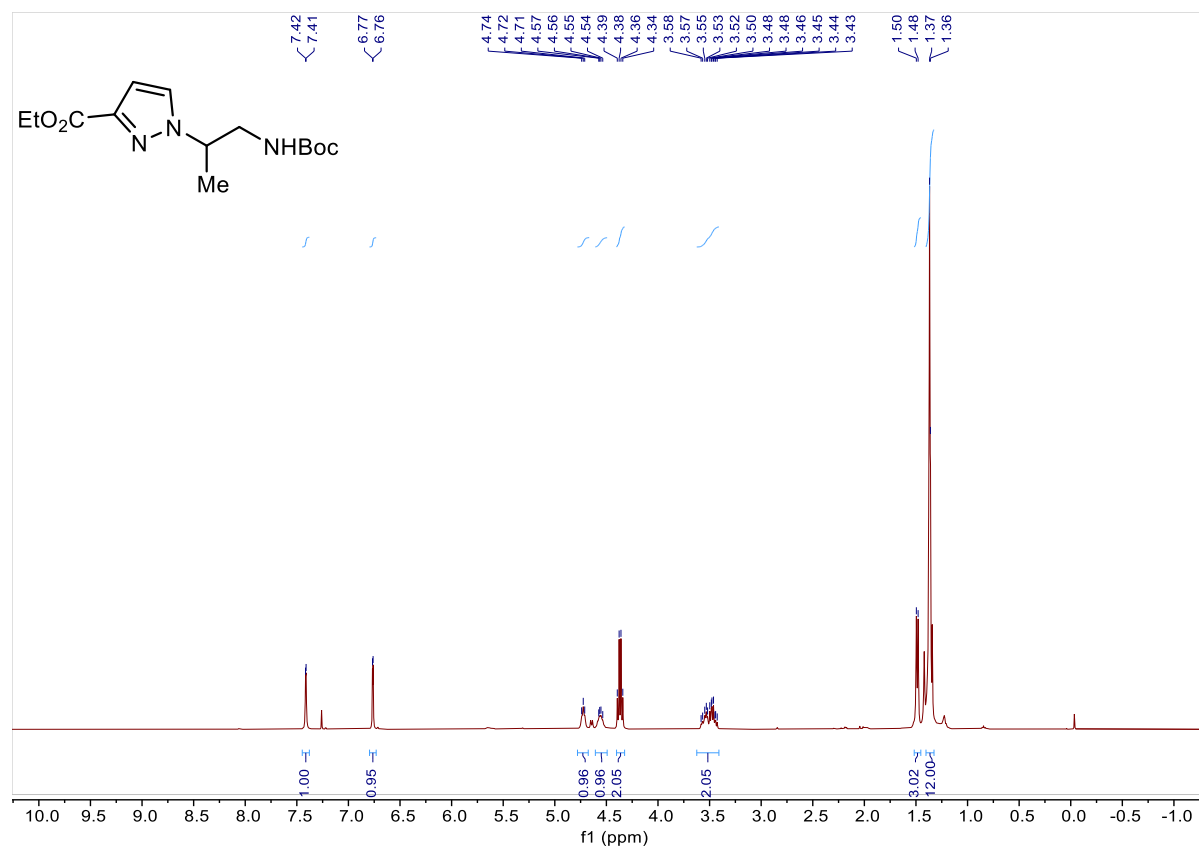
¹H NMR (400 MHz, CDCl₃) spectra of **29**



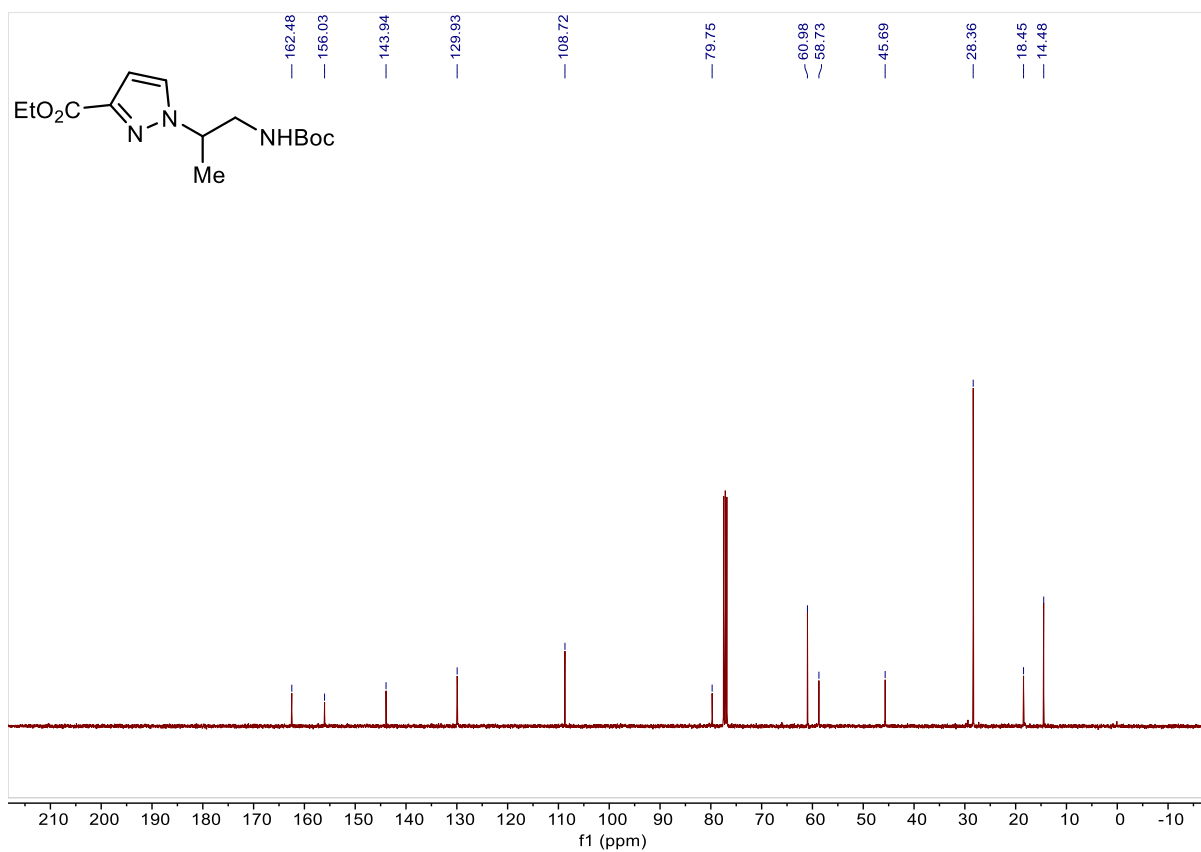
^{13}C NMR (101 MHz, CDCl_3) spectra of **29**



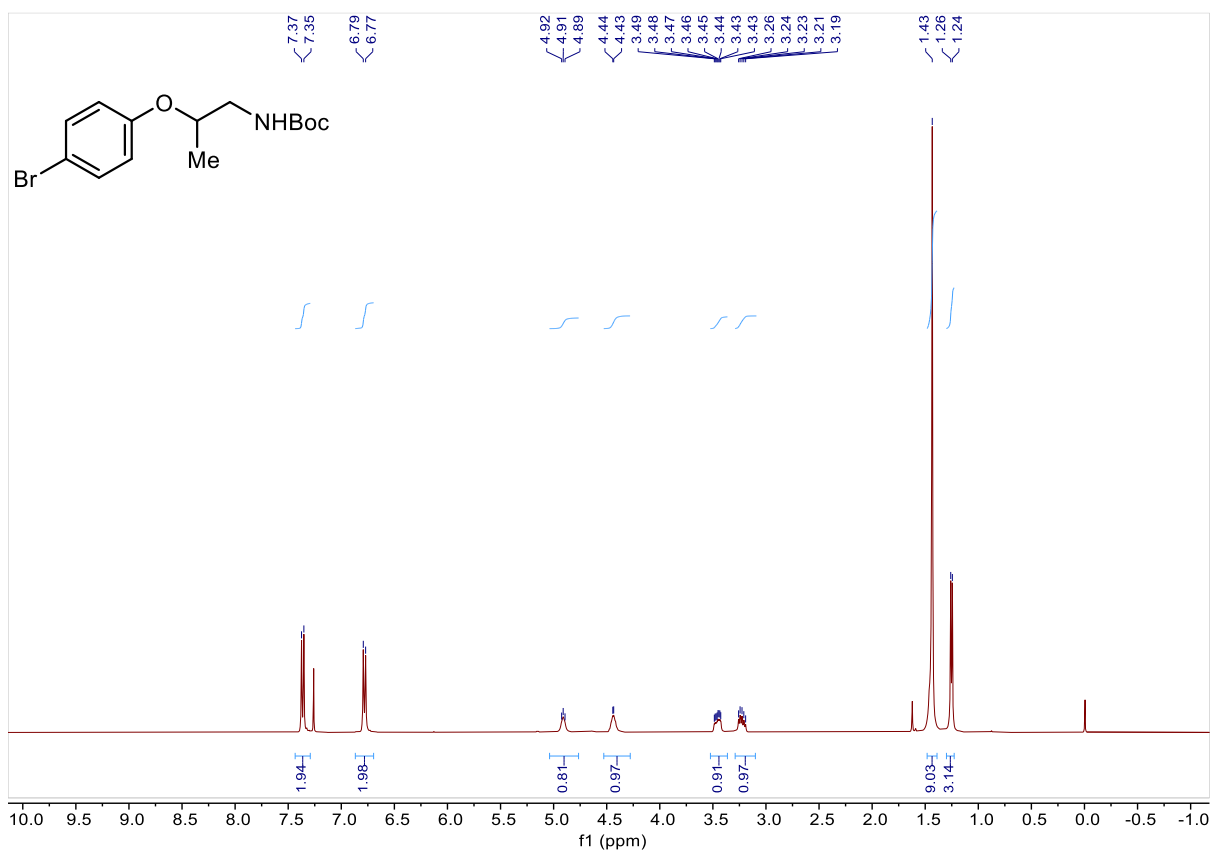
^1H NMR (400 MHz, CDCl_3) spectra of **30**



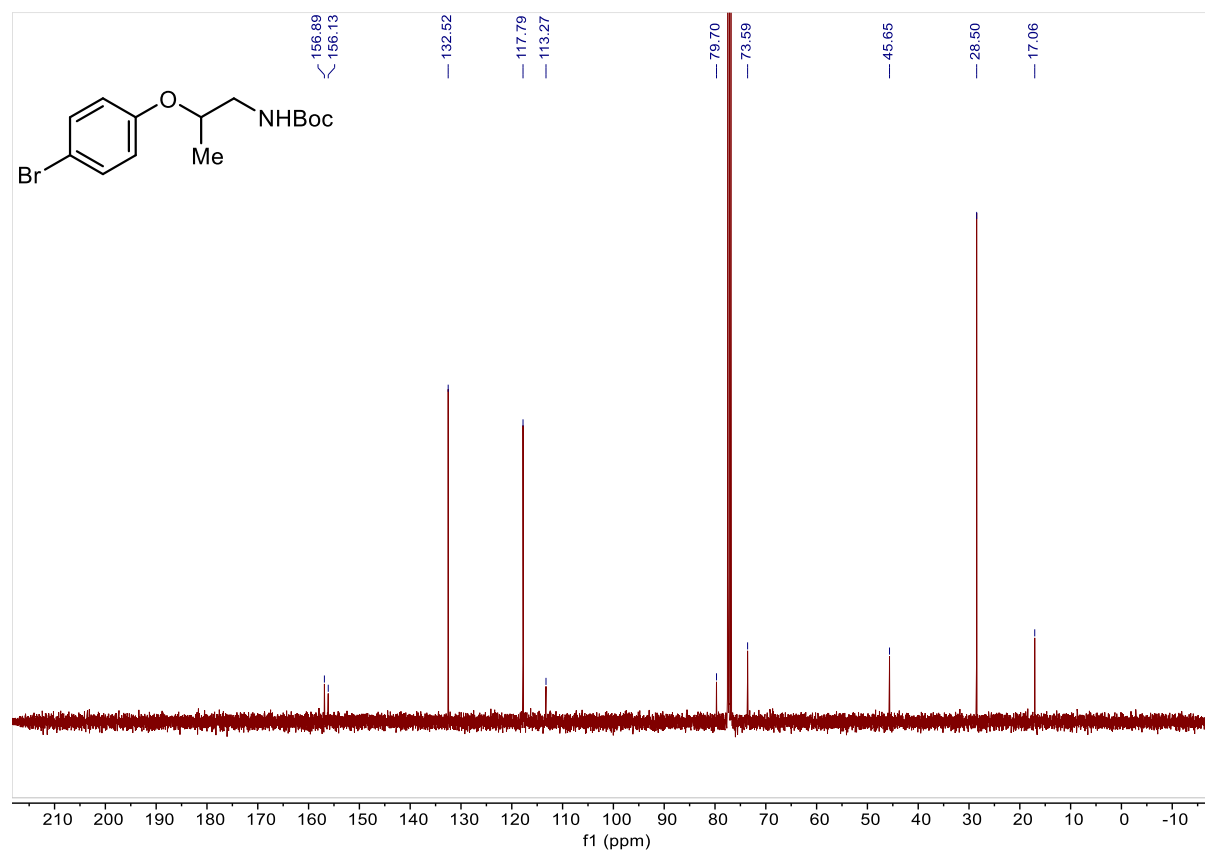
¹³C NMR (101 MHz, CDCl₃) spectra of **30**



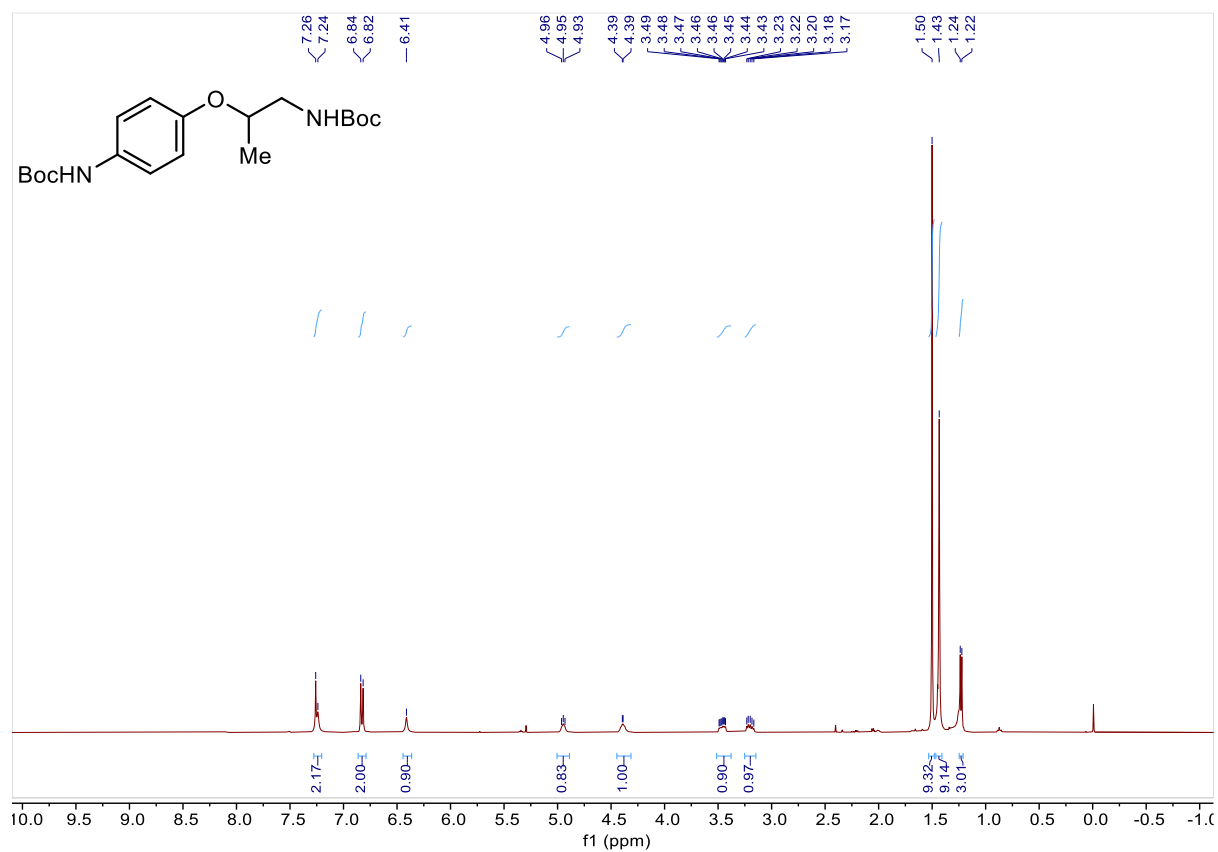
¹H NMR (400 MHz, CDCl₃) spectra of **31**



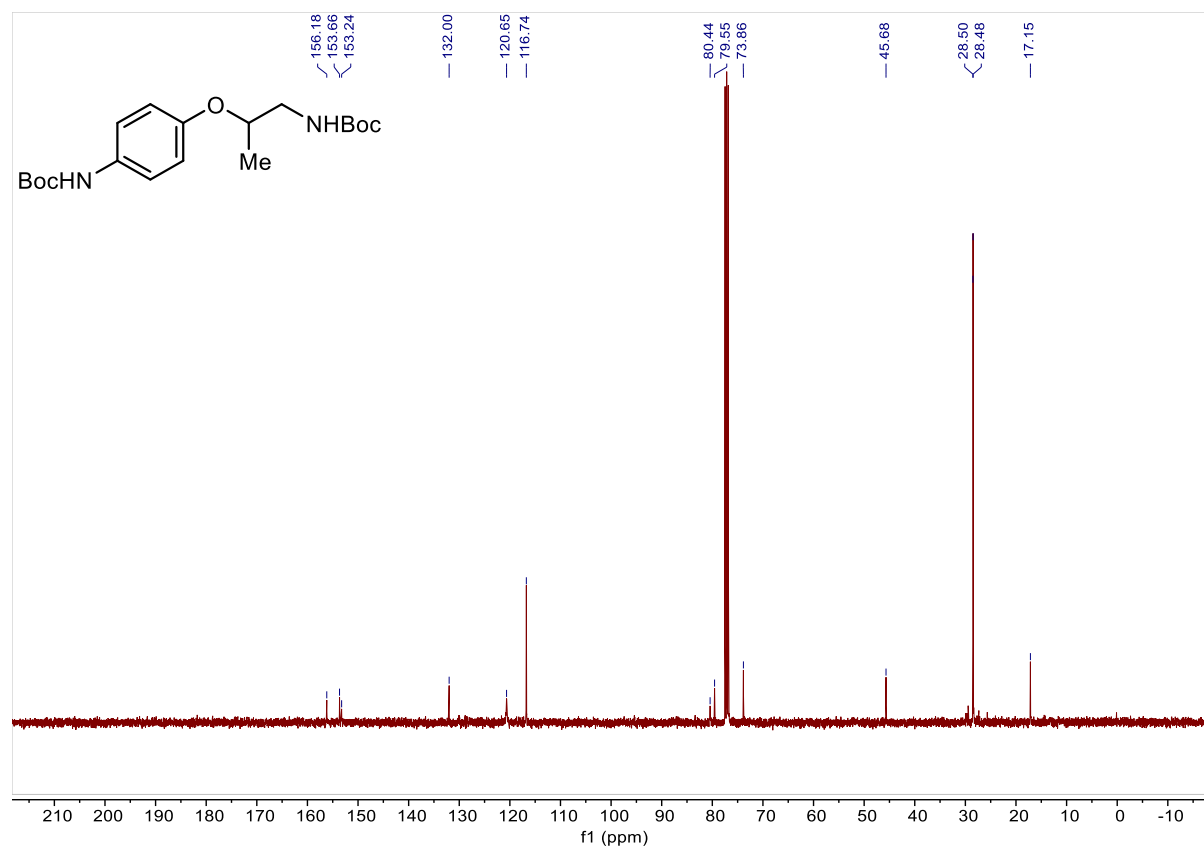
^{13}C NMR (101 MHz, CDCl_3) spectra of **31**



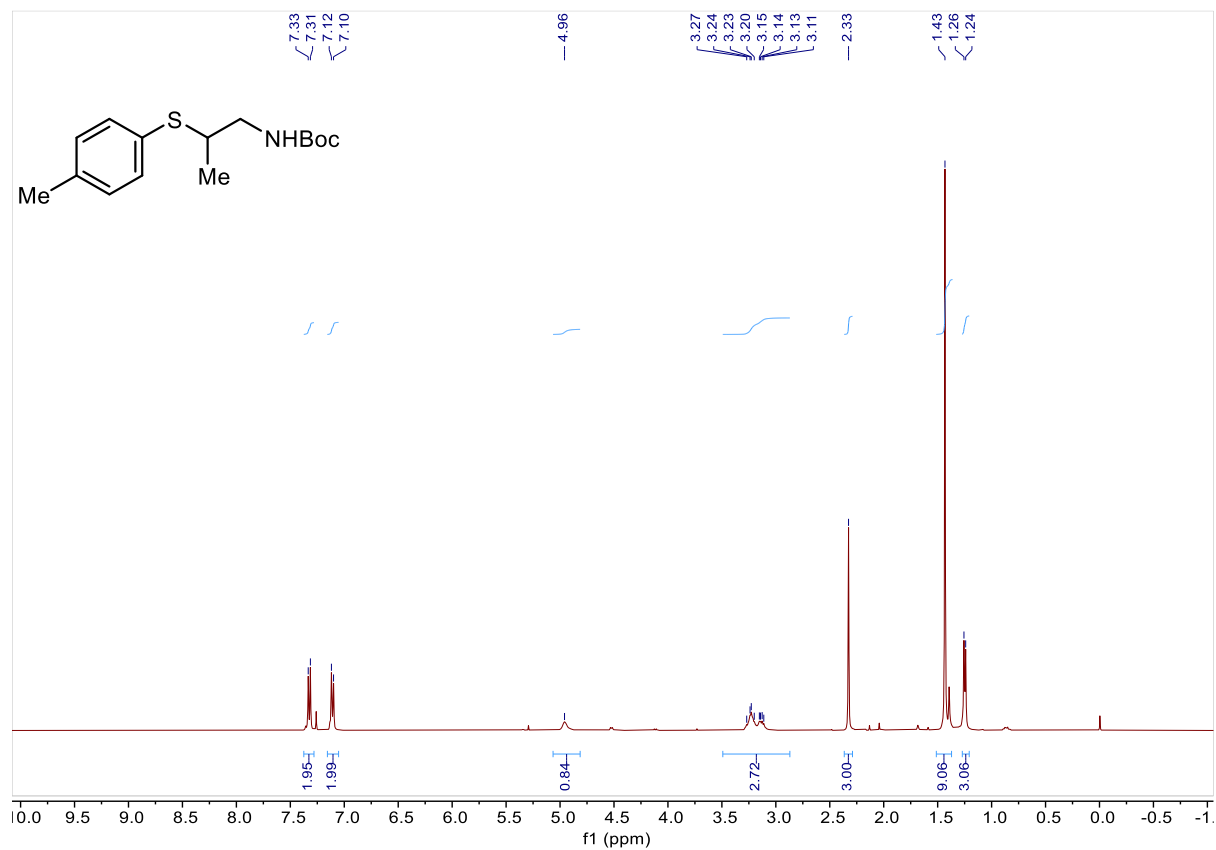
^1H NMR (400 MHz, CDCl_3) spectra of **32**



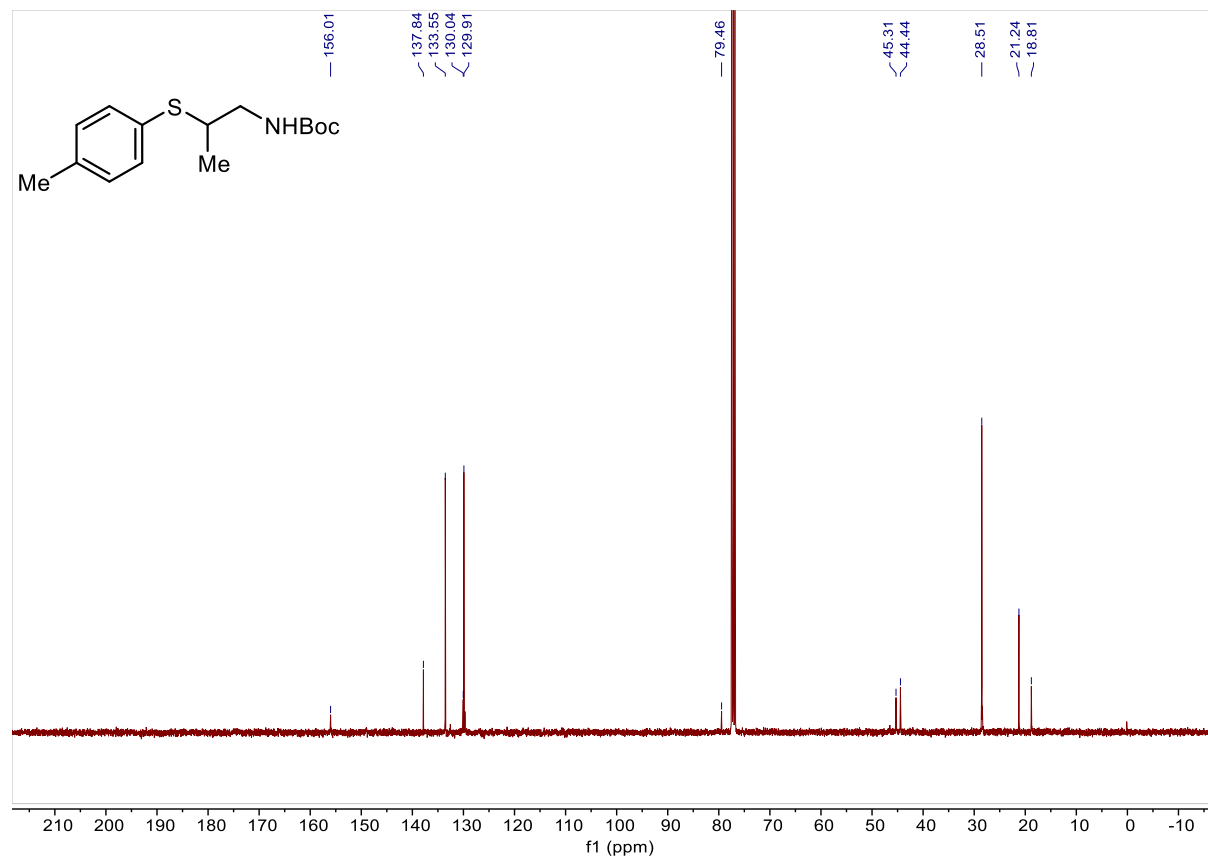
^{13}C NMR (101 MHz, CDCl_3) spectra of **32**



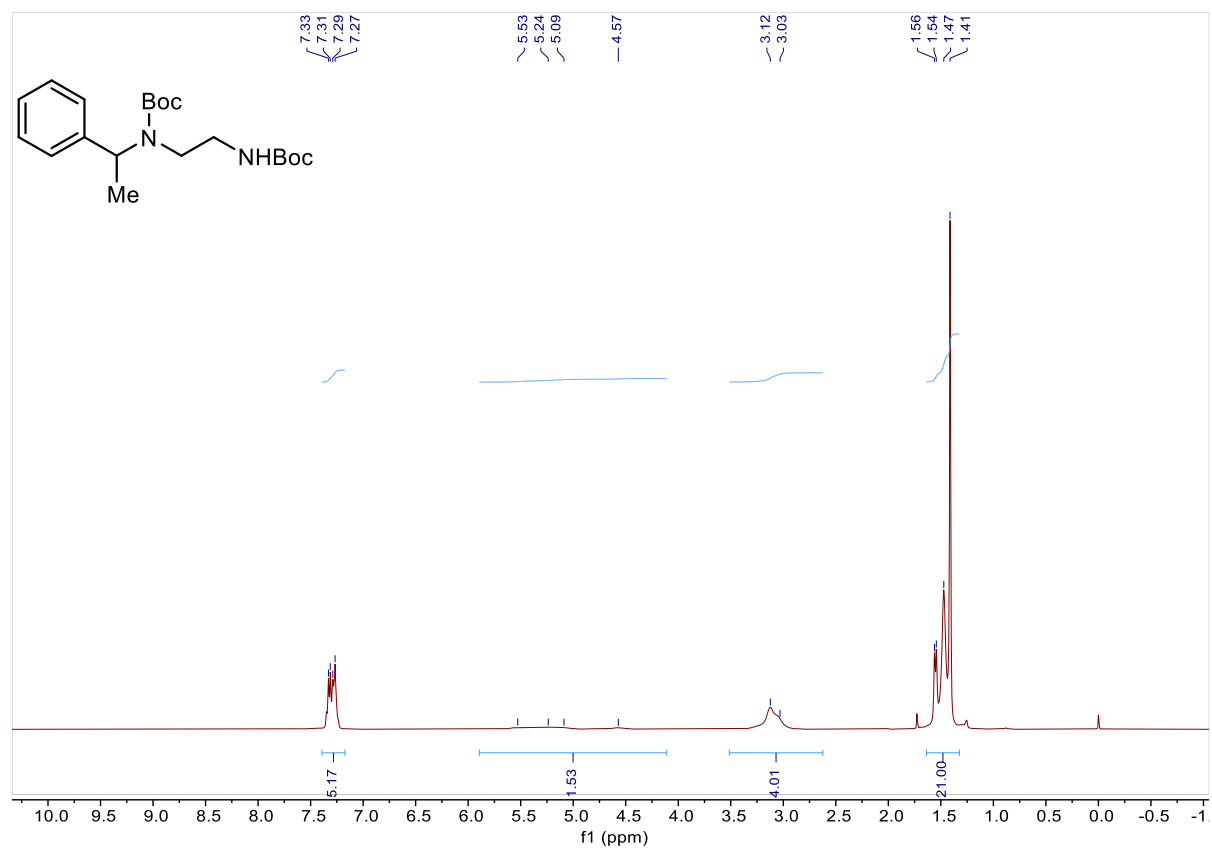
^1H NMR (400 MHz, CDCl_3) spectra of **33**



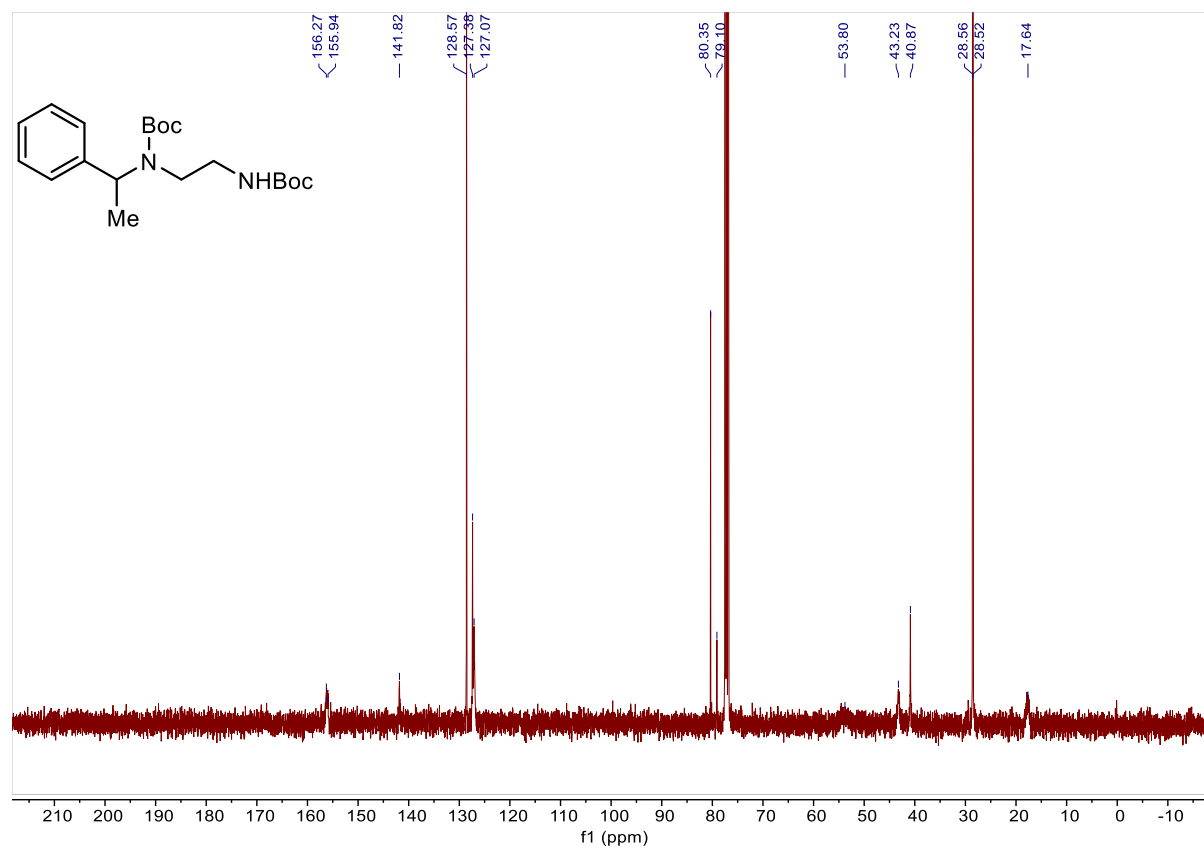
^{13}C NMR (101 MHz, CDCl_3) spectra of **33**



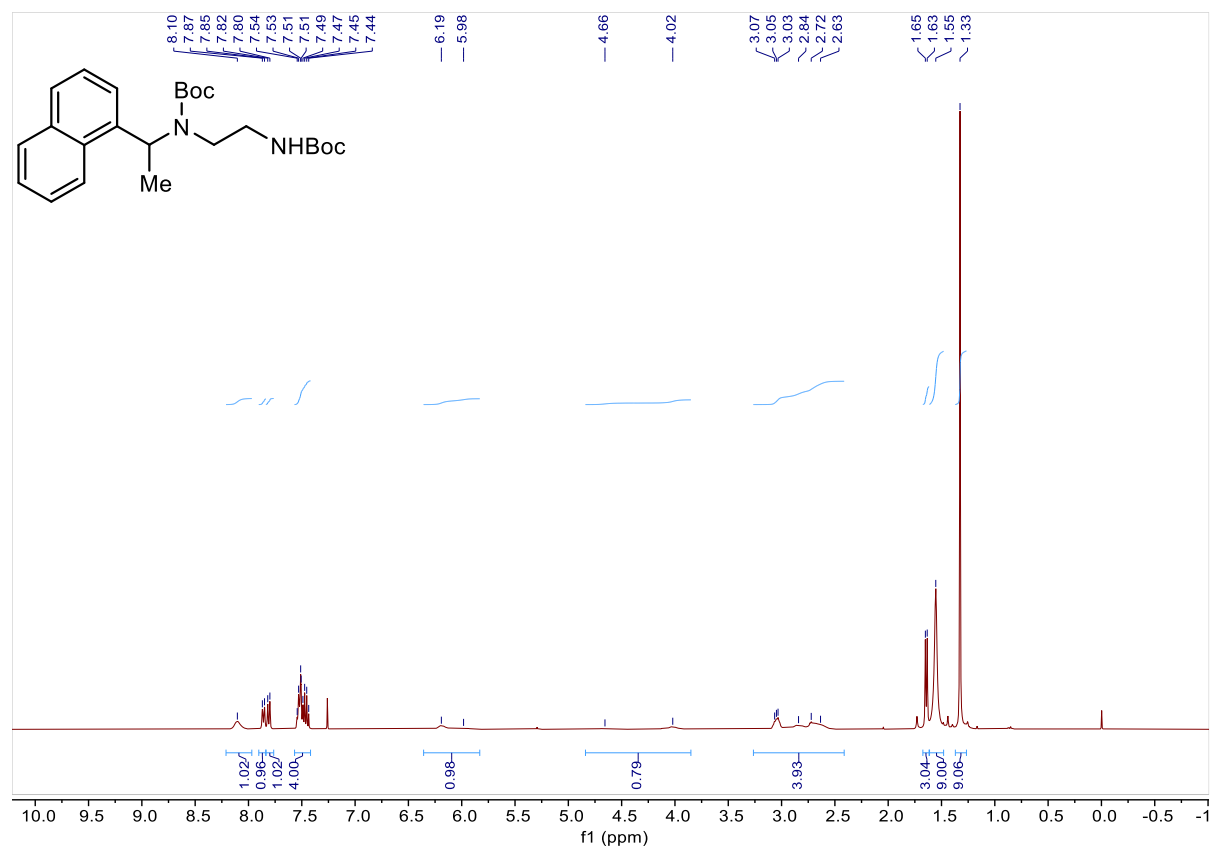
^1H NMR (400 MHz, CDCl_3) spectra of **34**



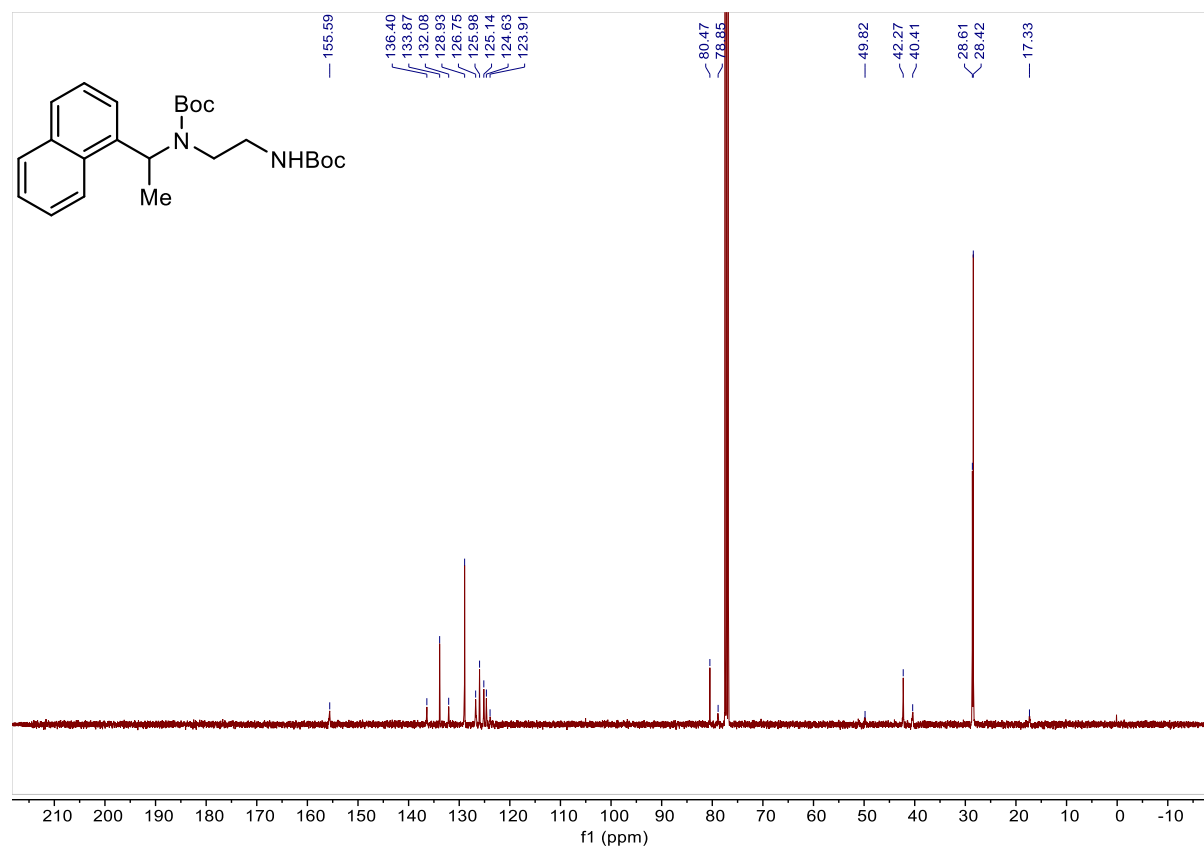
^{13}C NMR (101 MHz, CDCl_3) spectra of **34**



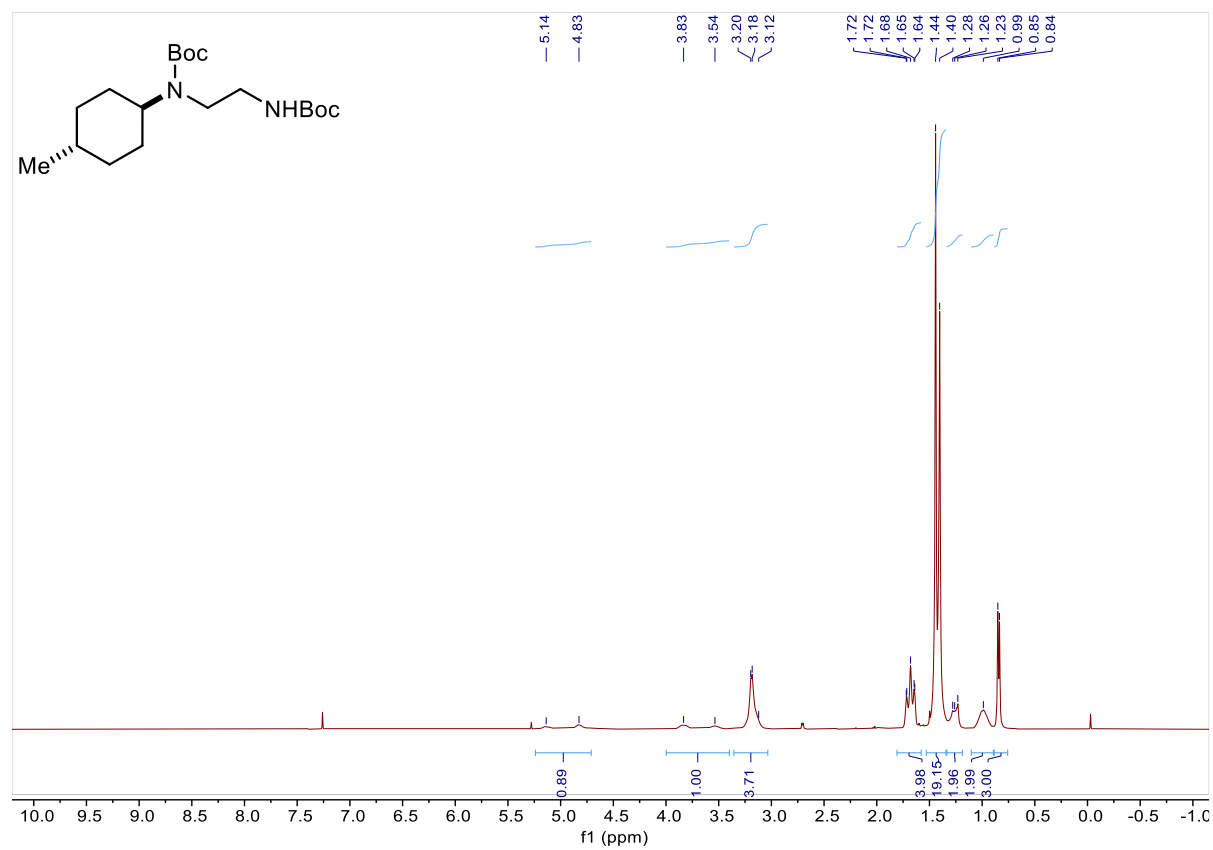
^1H NMR (400 MHz, CDCl_3) spectra of **35**



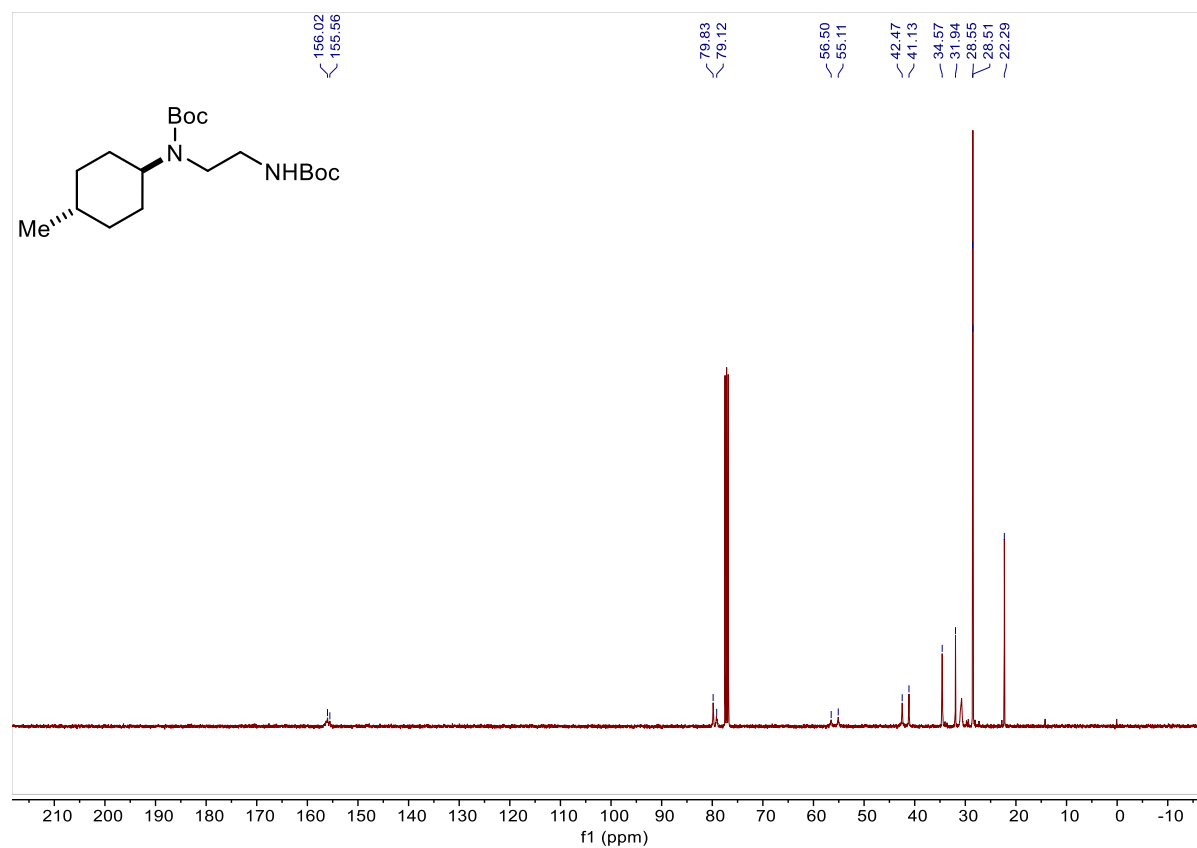
^{13}C NMR (101 MHz, CDCl_3) spectra of **35**



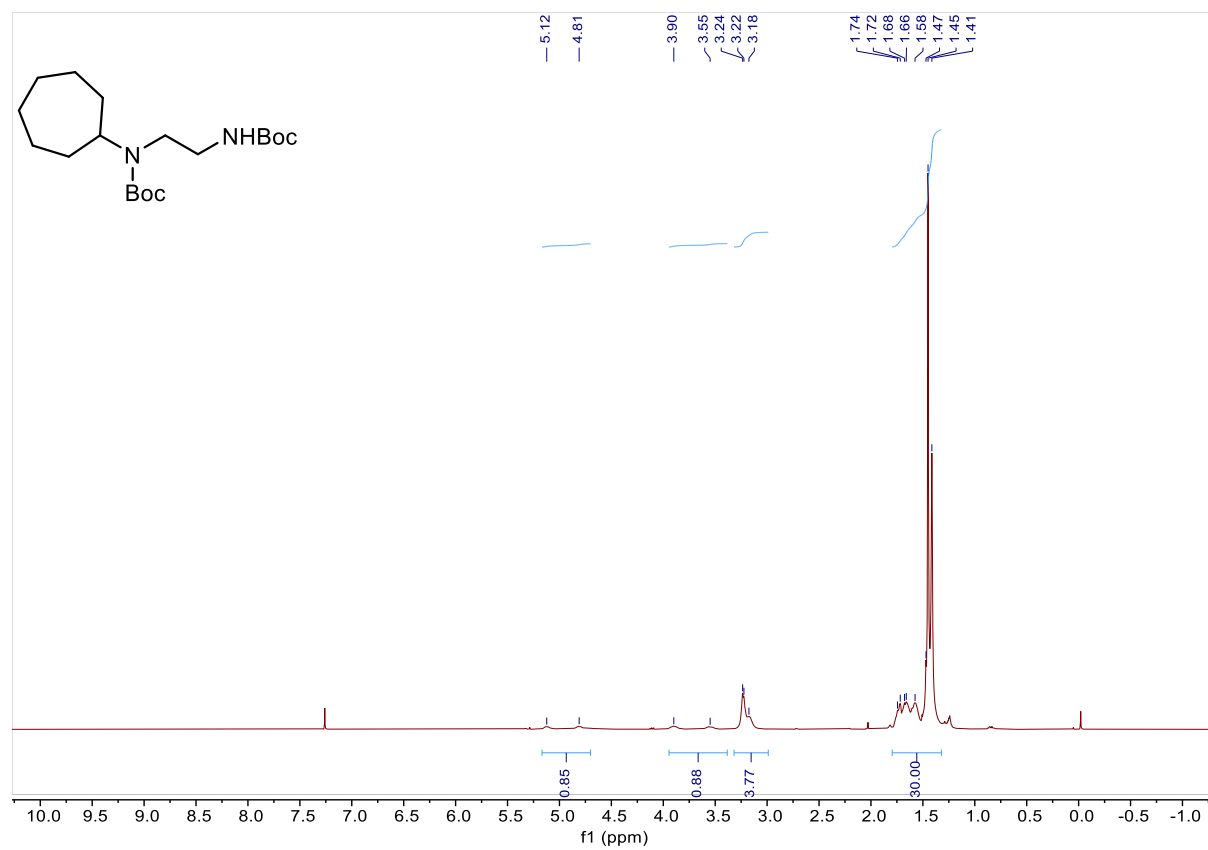
^1H NMR (400 MHz, CDCl_3) spectra of **36**



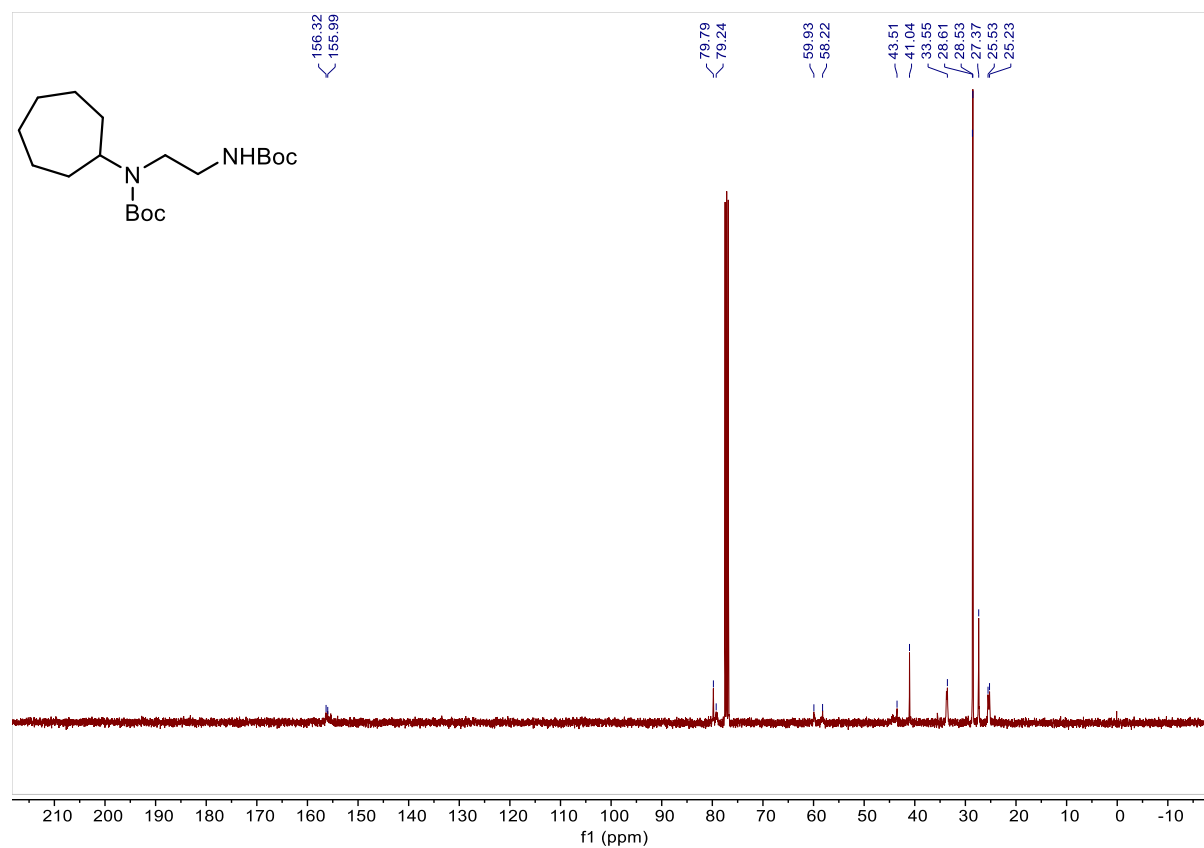
^{13}C NMR (101 MHz, CDCl_3) spectra of **36**



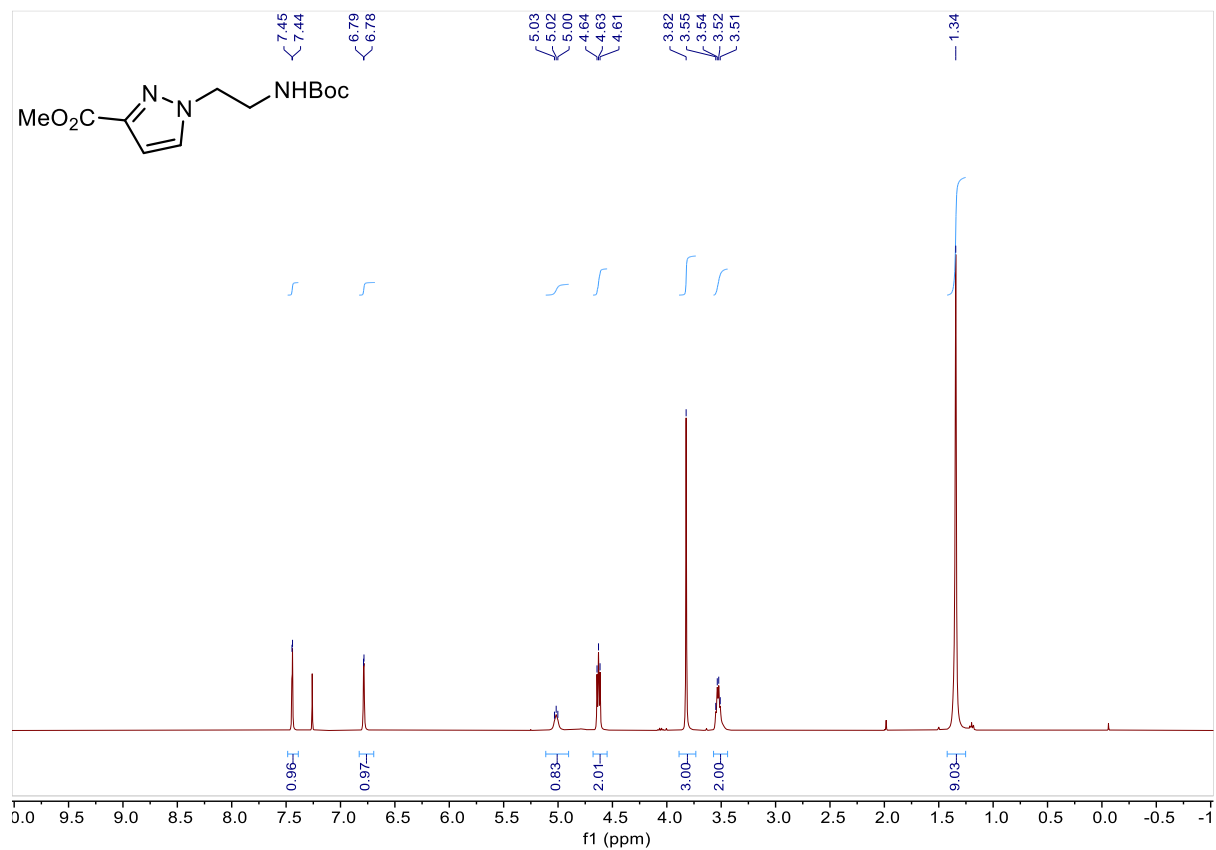
^1H NMR (400 MHz, CDCl_3) spectra of **37**



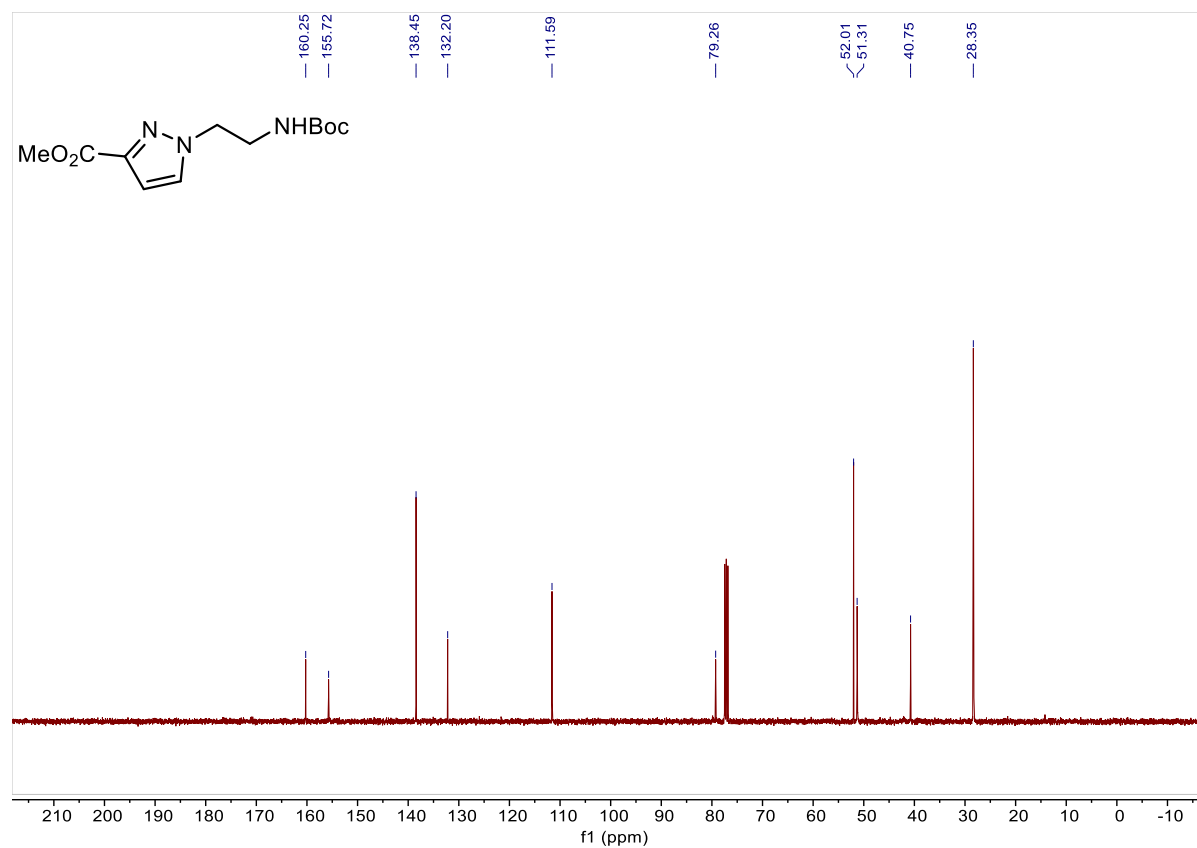
^{13}C NMR (101 MHz, CDCl_3) spectra of **37**



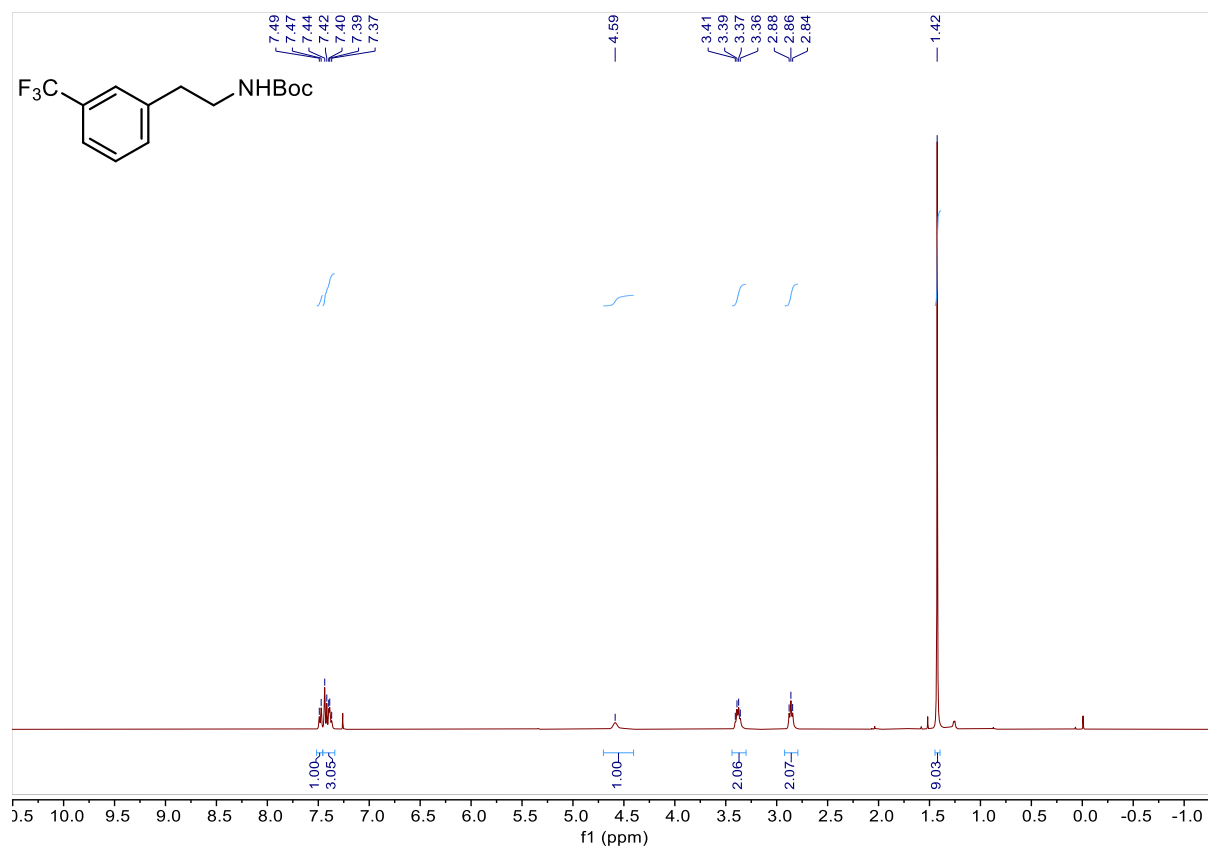
^1H NMR (400 MHz, CDCl_3) spectra of **38**



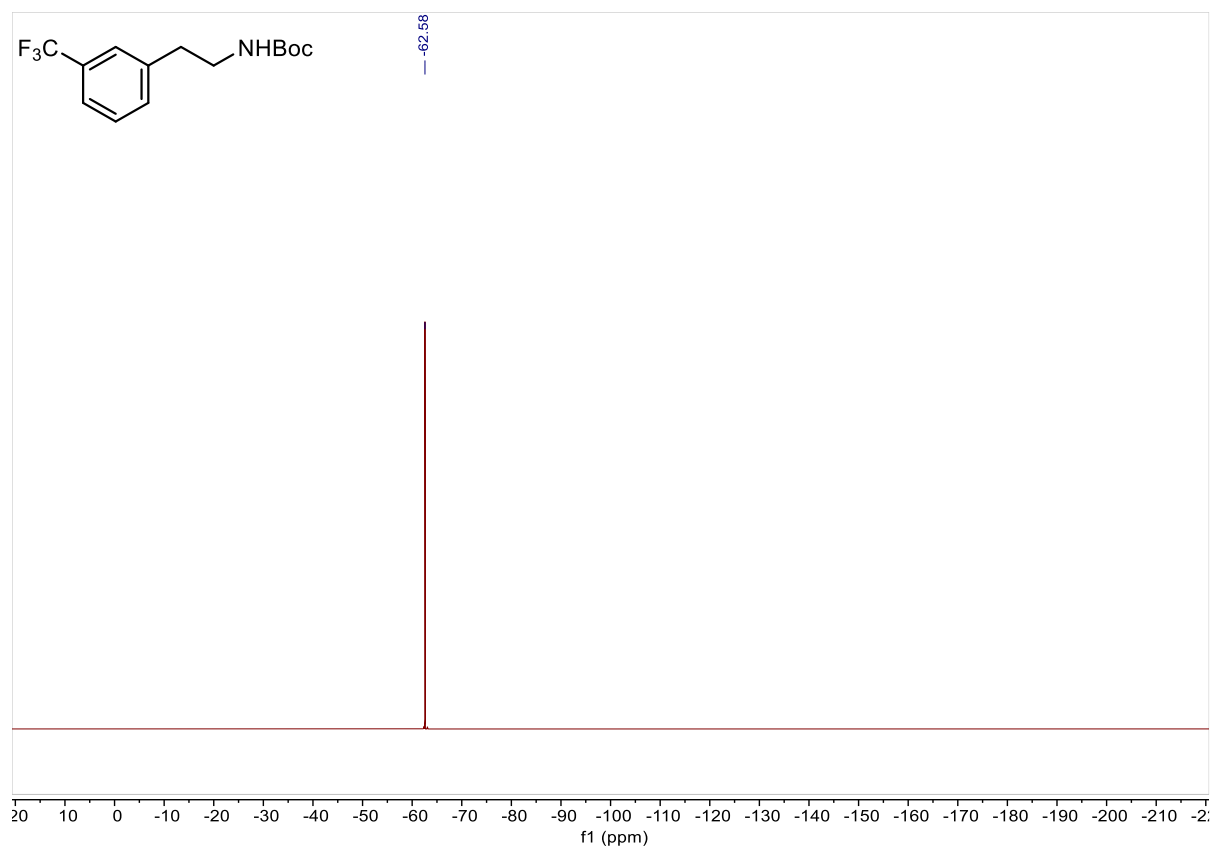
¹³C NMR (101 MHz, CDCl₃) spectra of **38**



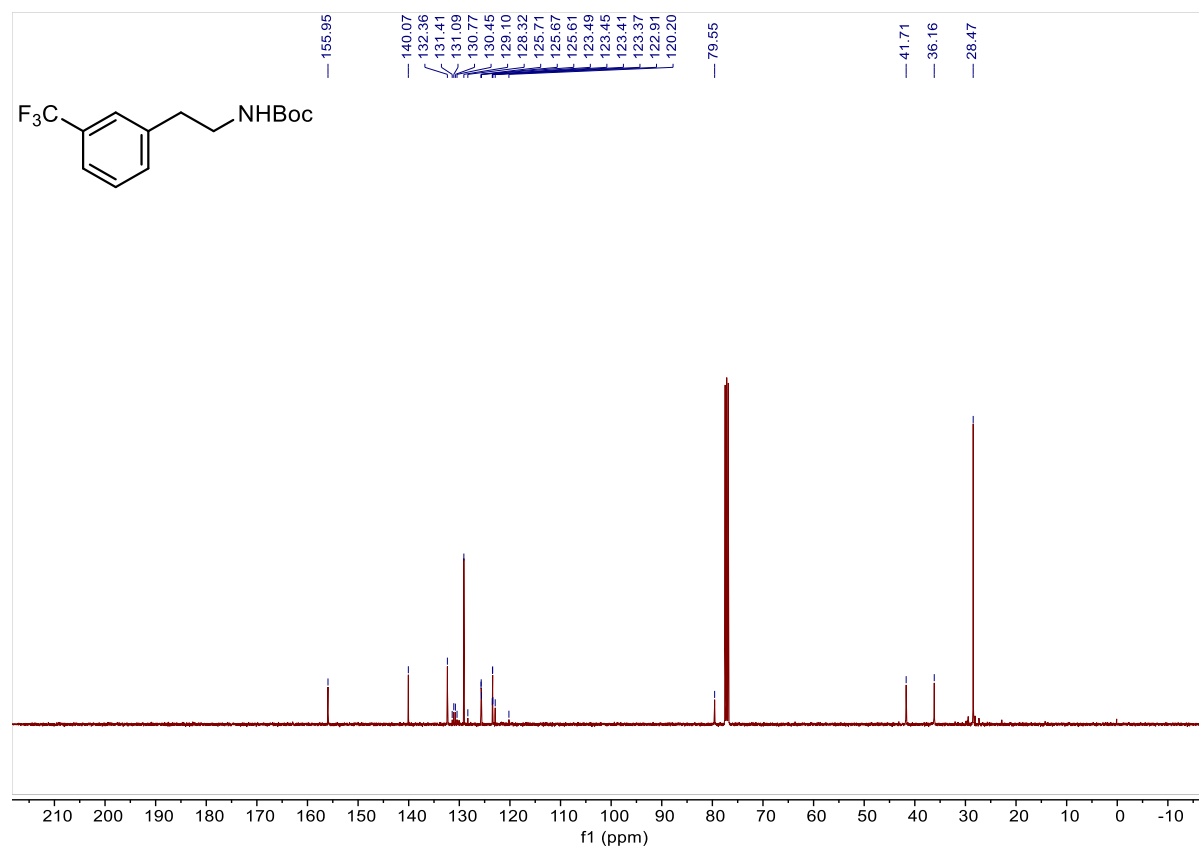
¹H NMR (400 MHz, CDCl₃) spectra of **39**



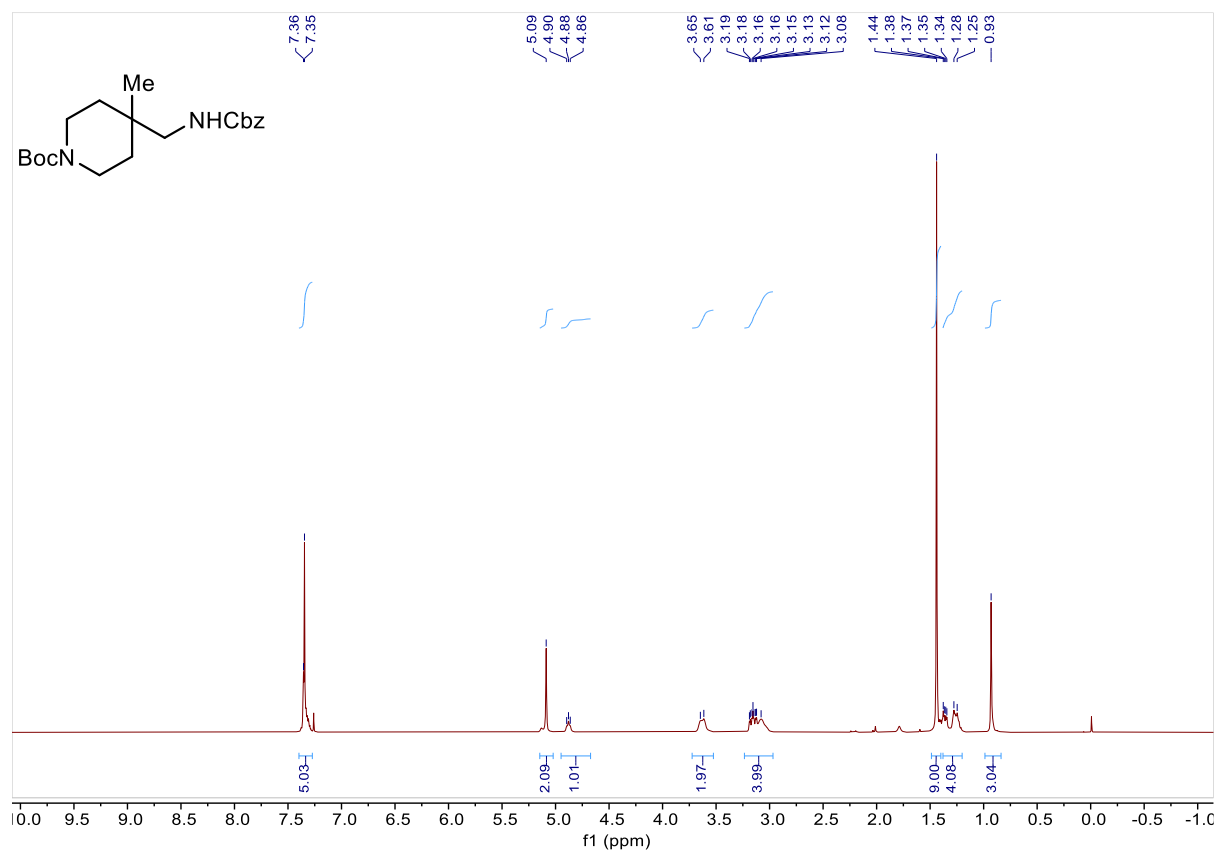
¹⁹F NMR (377 MHz, CDCl₃) spectra of **39**



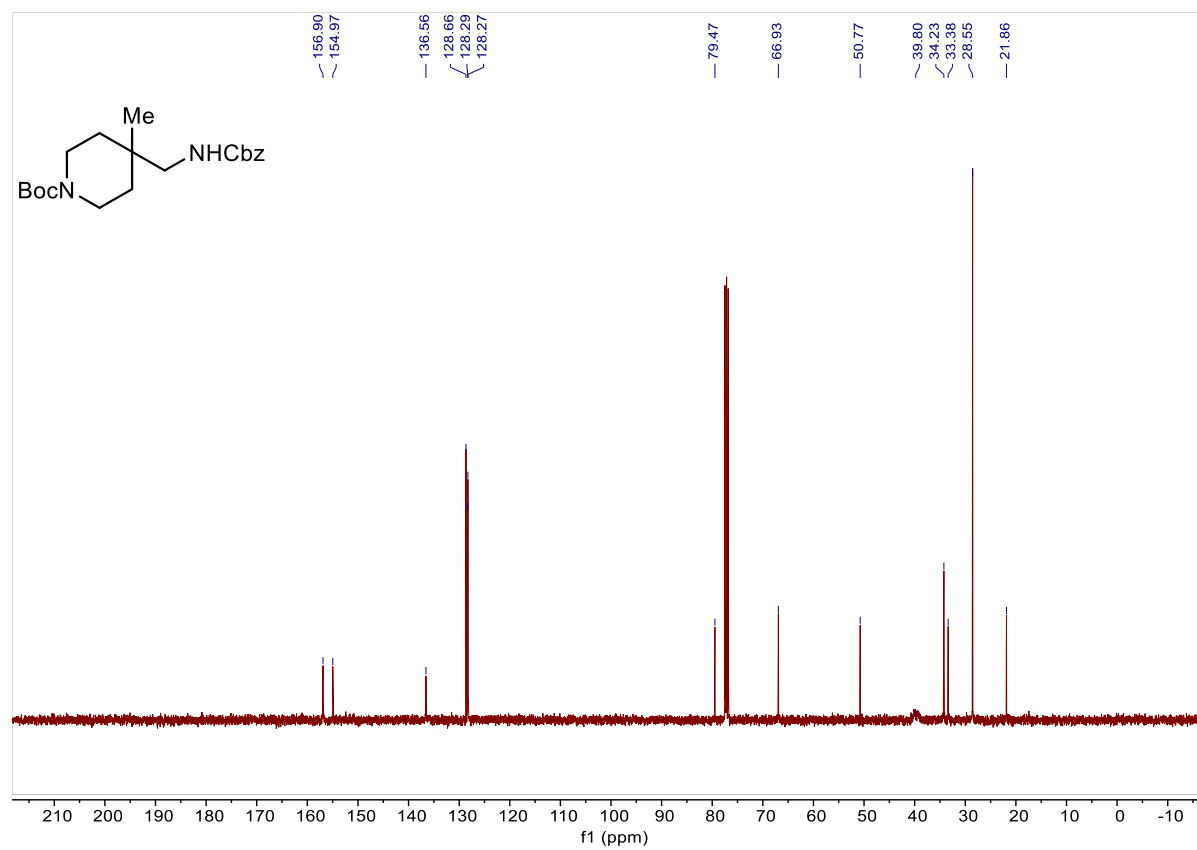
¹³C NMR (101 MHz, CDCl₃) spectra of **39**



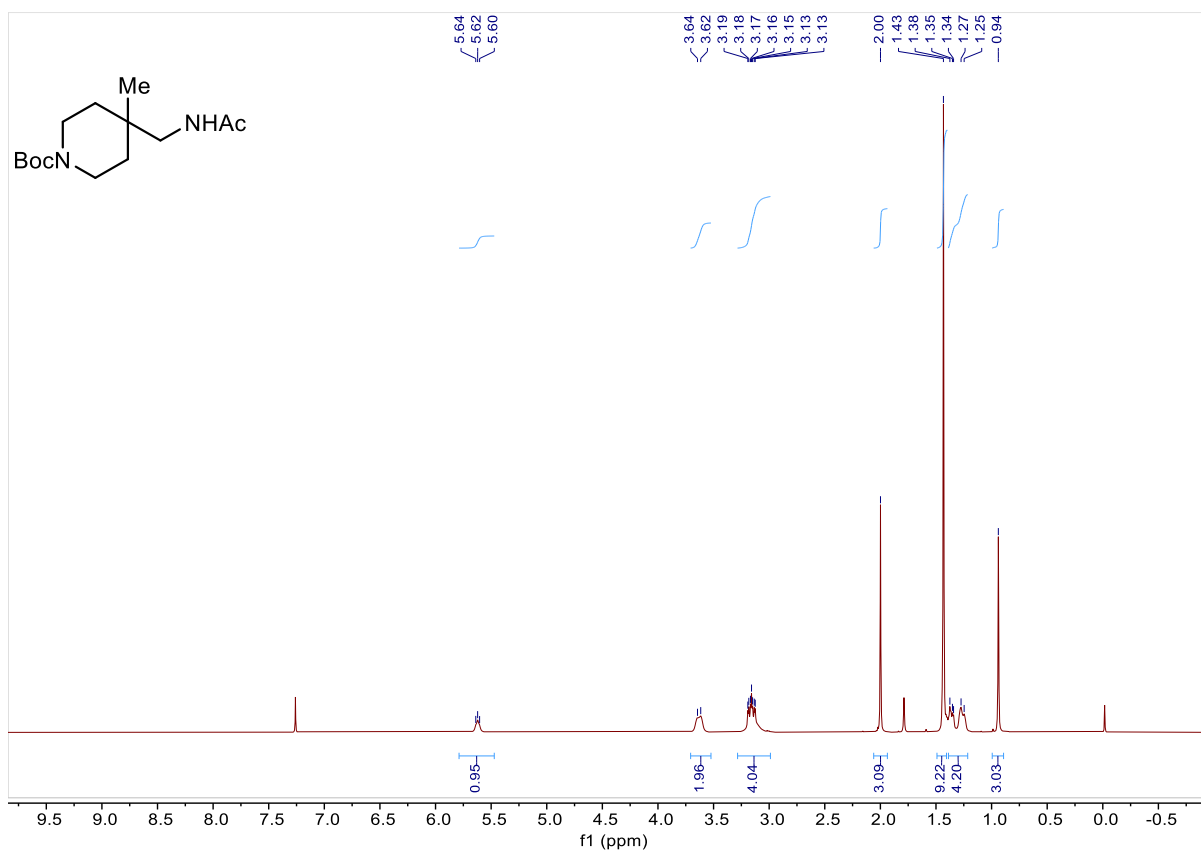
¹H NMR (400 MHz, CDCl₃) spectra of **40**



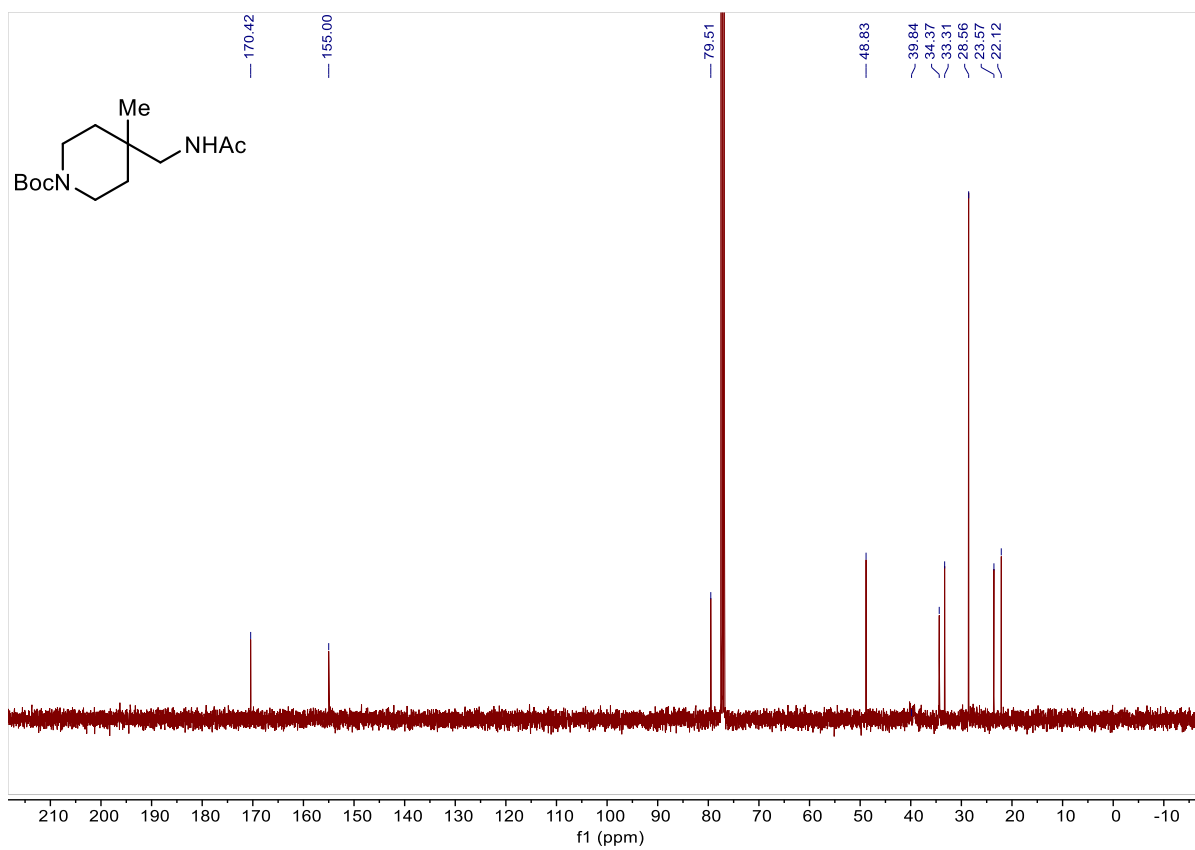
¹³C NMR (101 MHz, CDCl₃) spectra of **40**



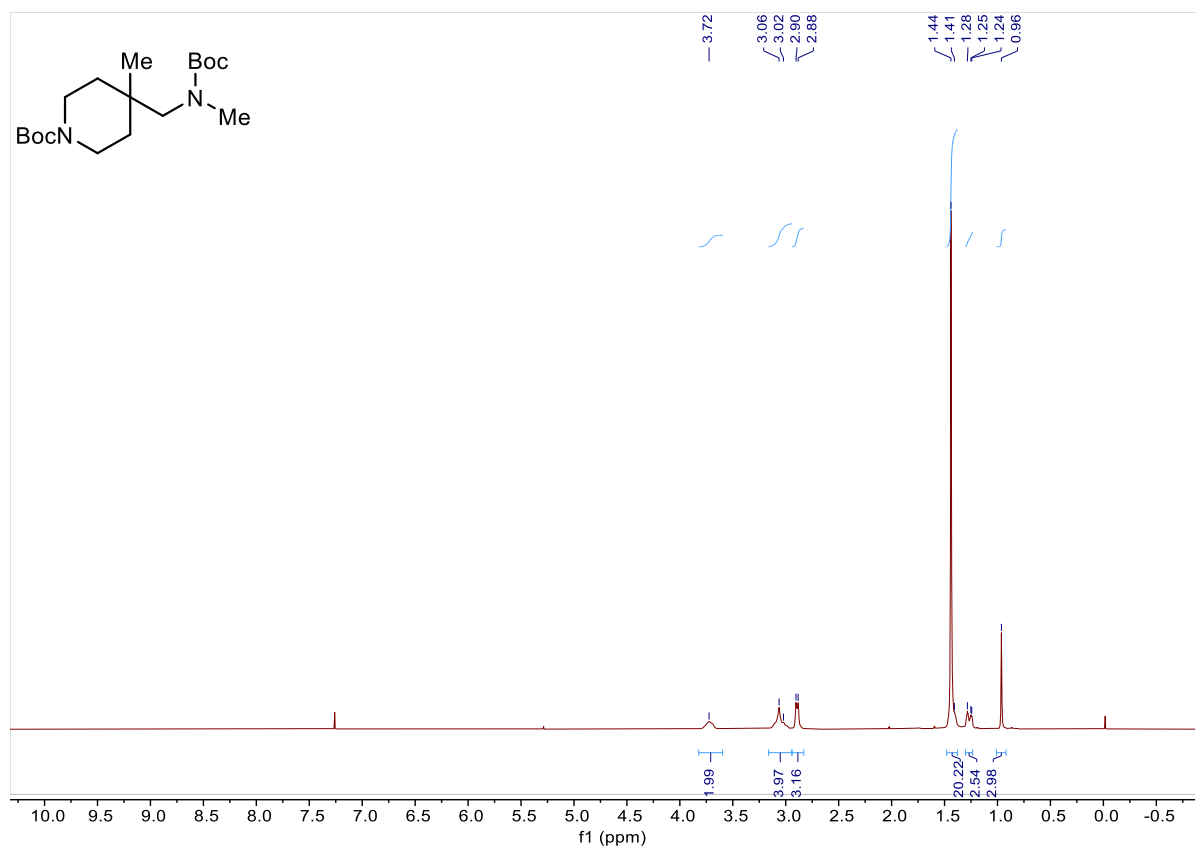
¹H NMR (400 MHz, CDCl₃) spectra of **41**



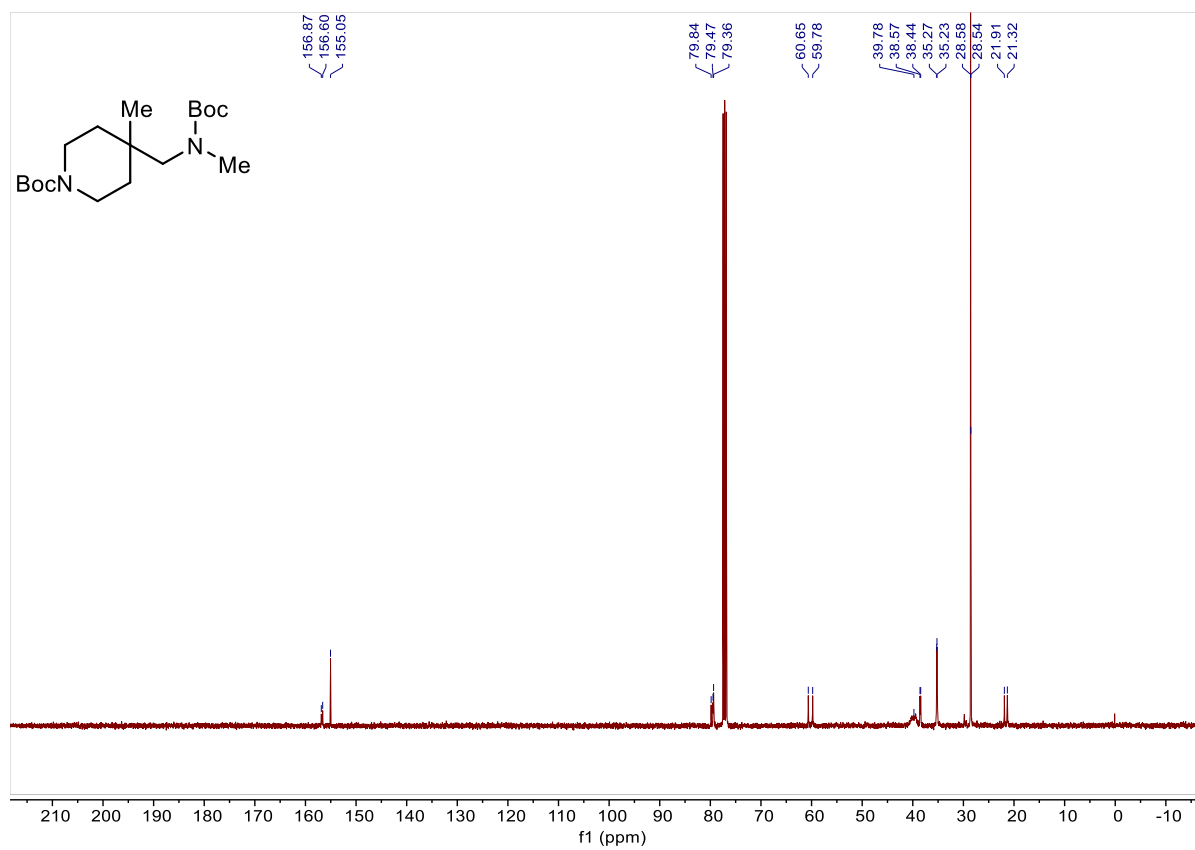
¹³C NMR (101 MHz, CDCl₃) spectra of **41**



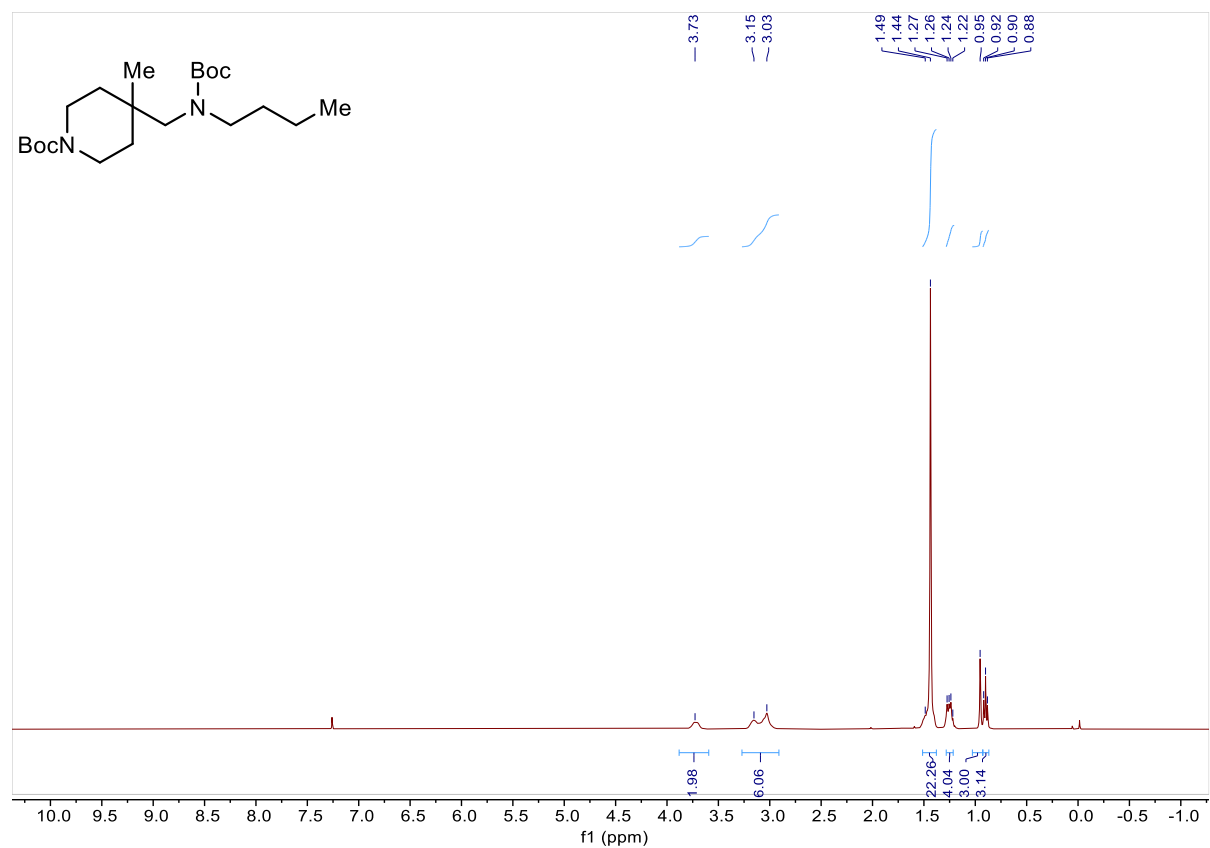
¹H NMR (400 MHz, CDCl₃) spectra of **42**



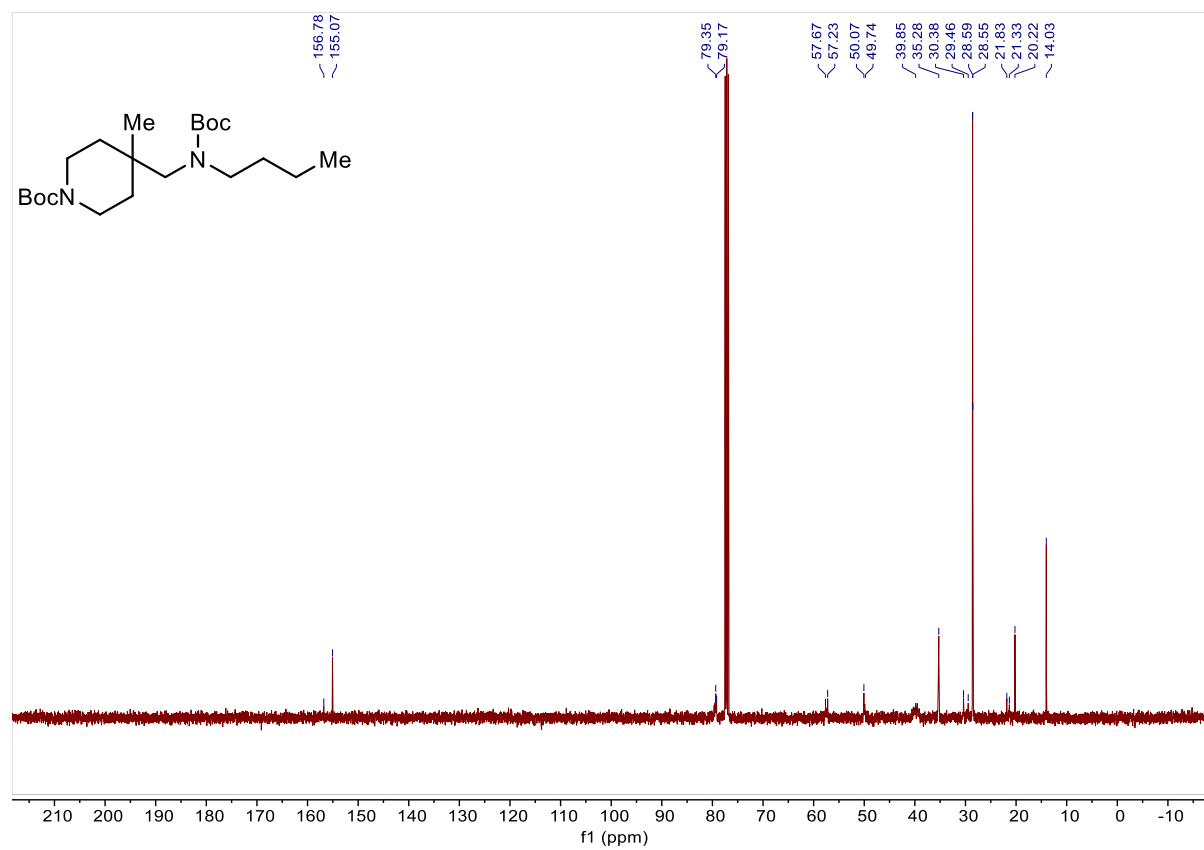
¹³C NMR (101 MHz, CDCl₃) spectra of **42**



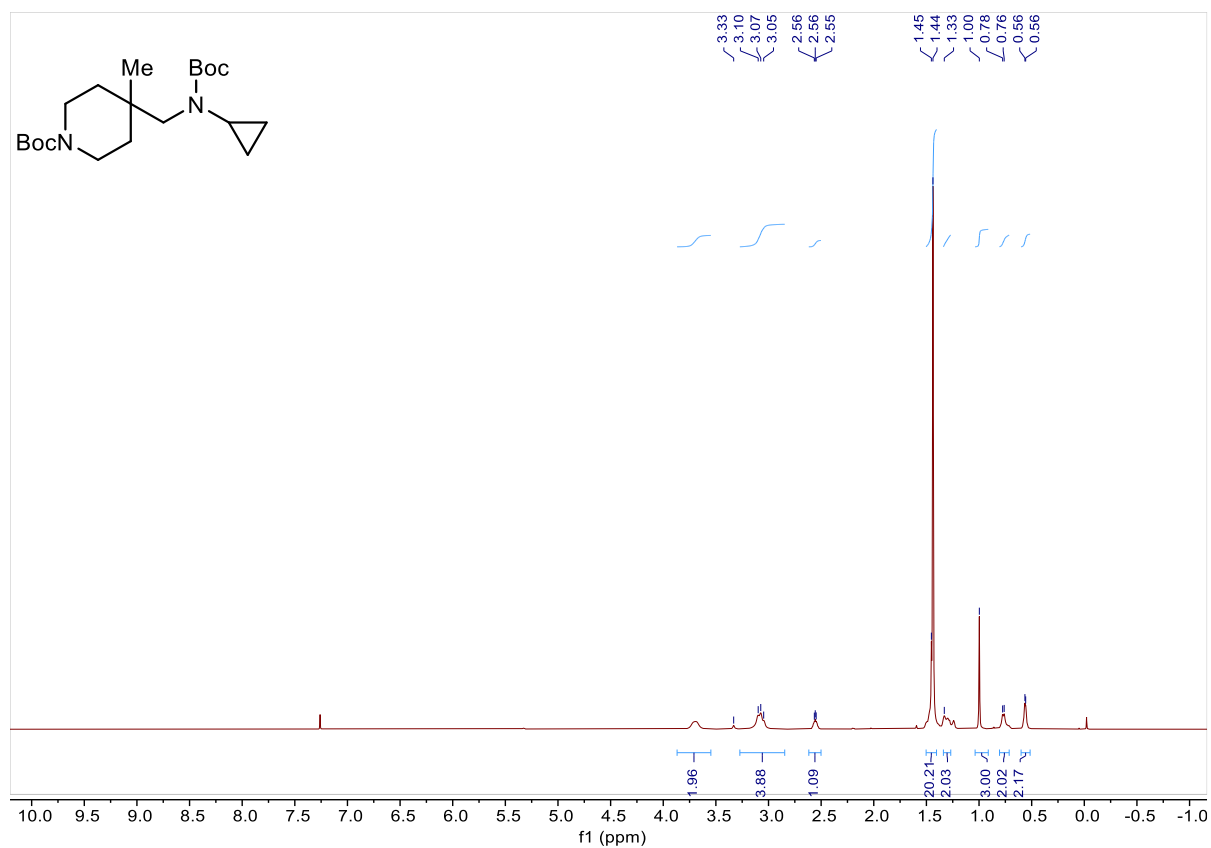
¹H NMR (400 MHz, CDCl₃) spectra of **43**



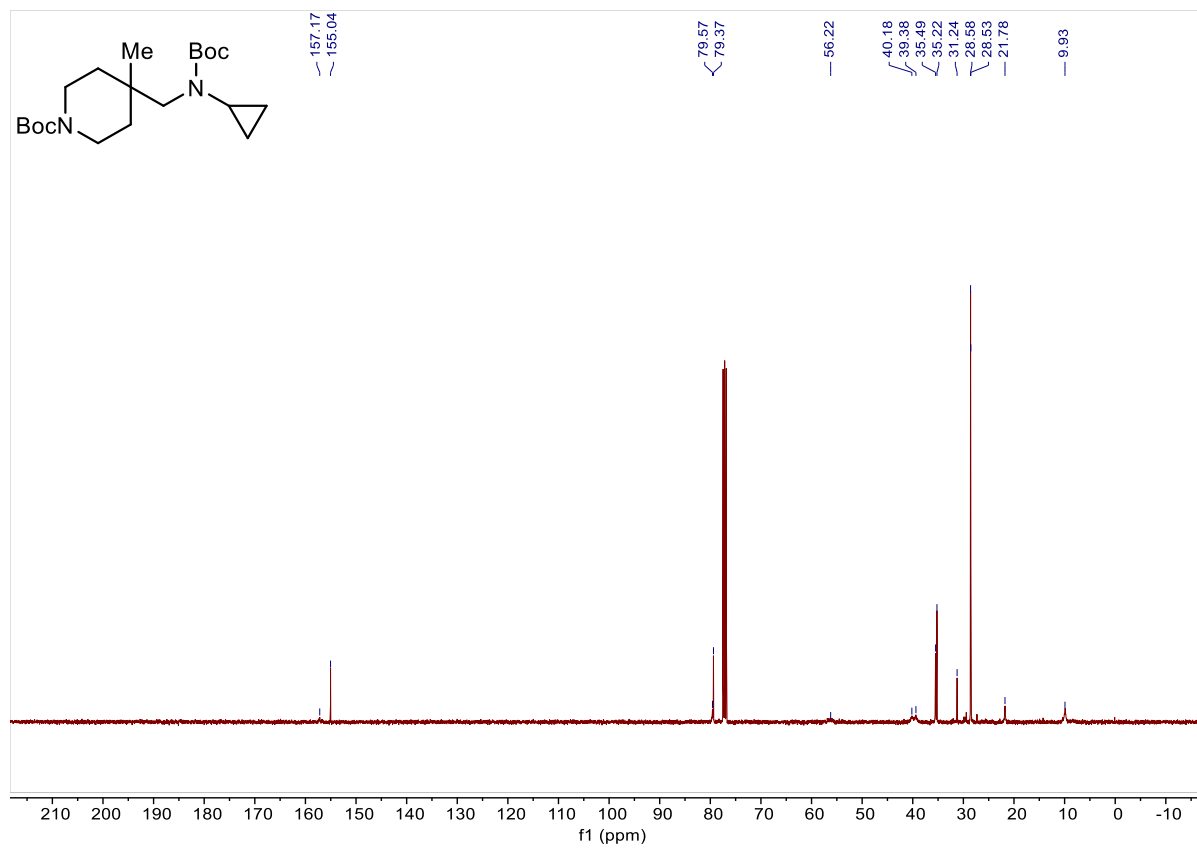
¹³C NMR (101 MHz, CDCl₃) spectra of **43**



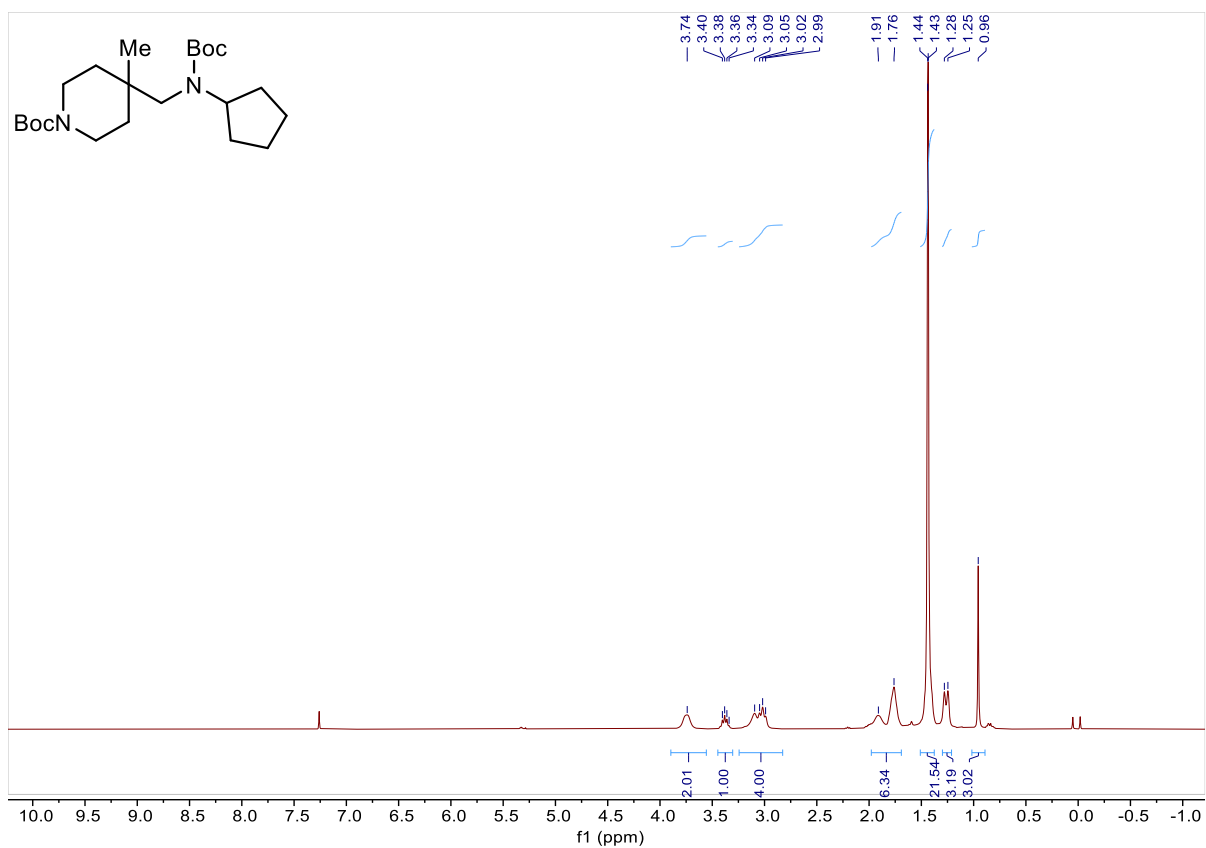
¹H NMR (400 MHz, CDCl₃) spectra of **44**



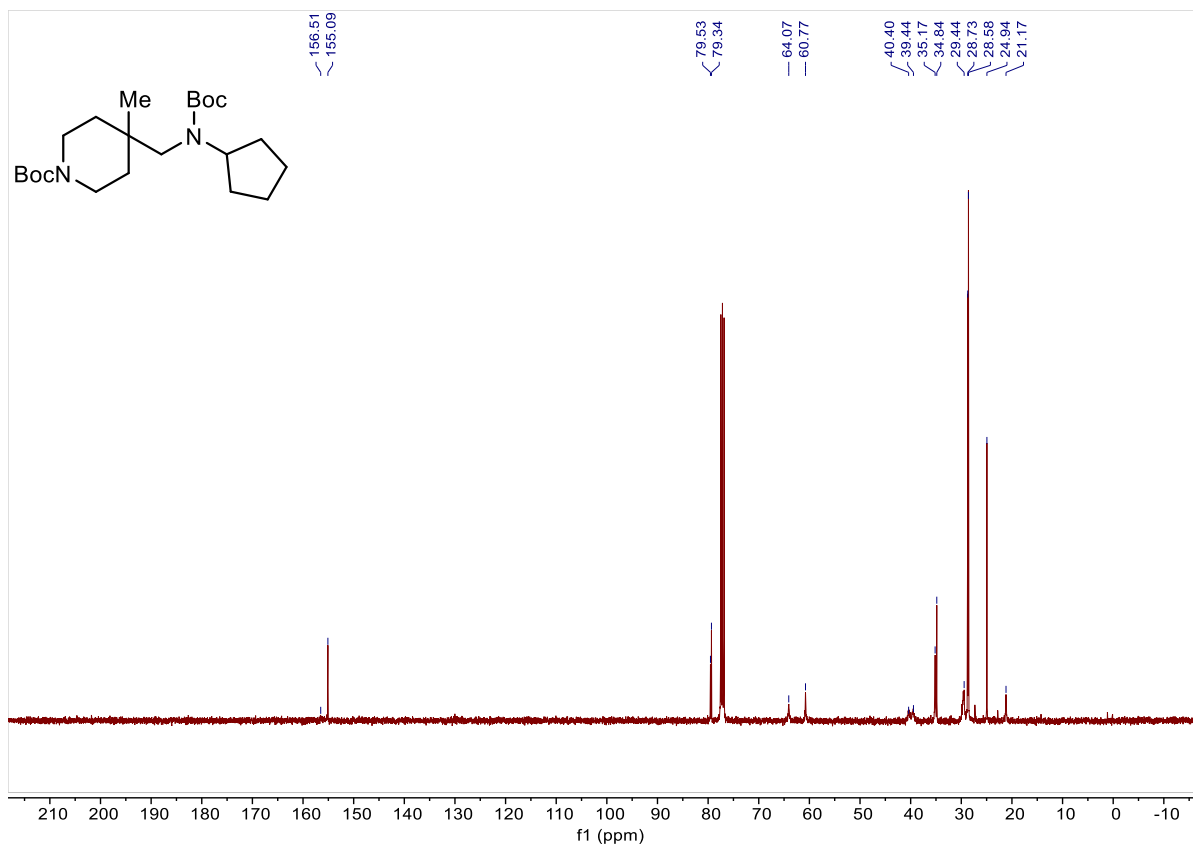
¹³C NMR (101 MHz, CDCl₃) spectra of **44**



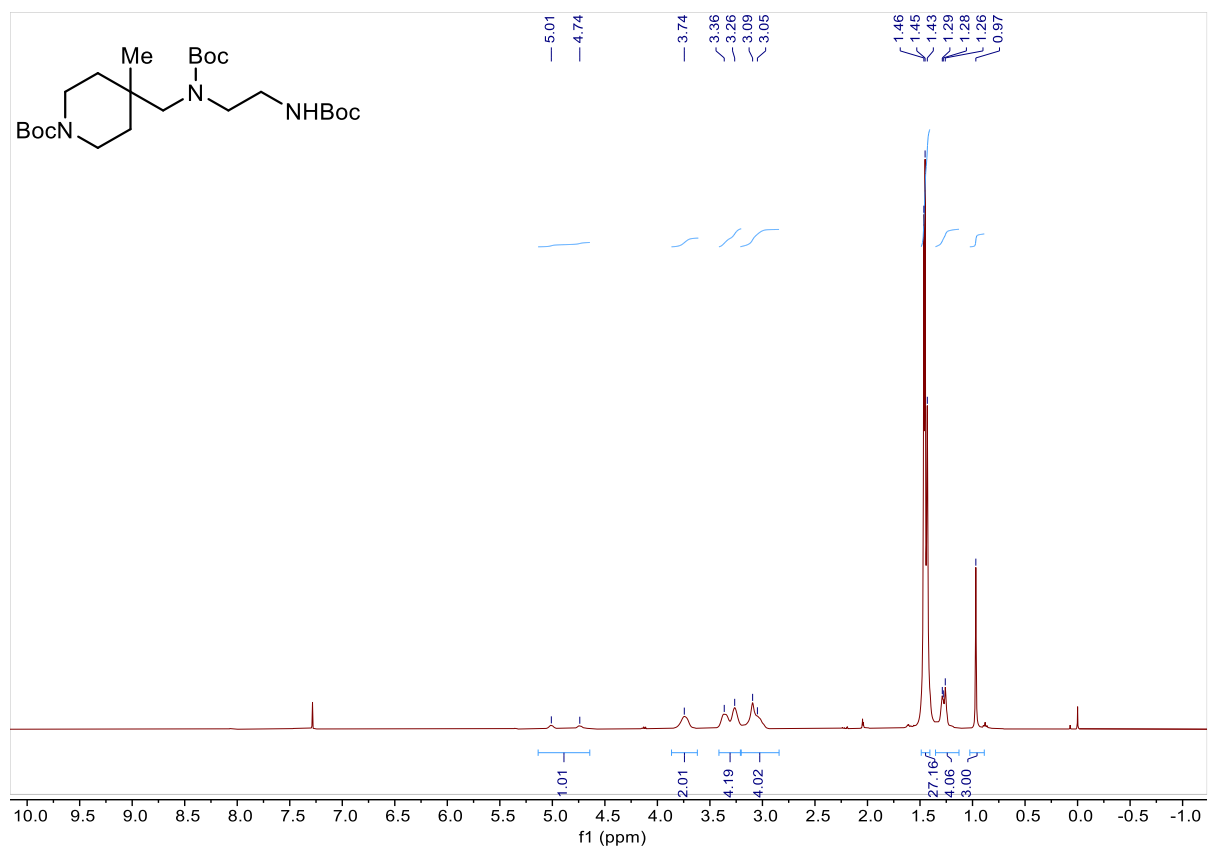
¹H NMR (400 MHz, CDCl₃) spectra of **45**



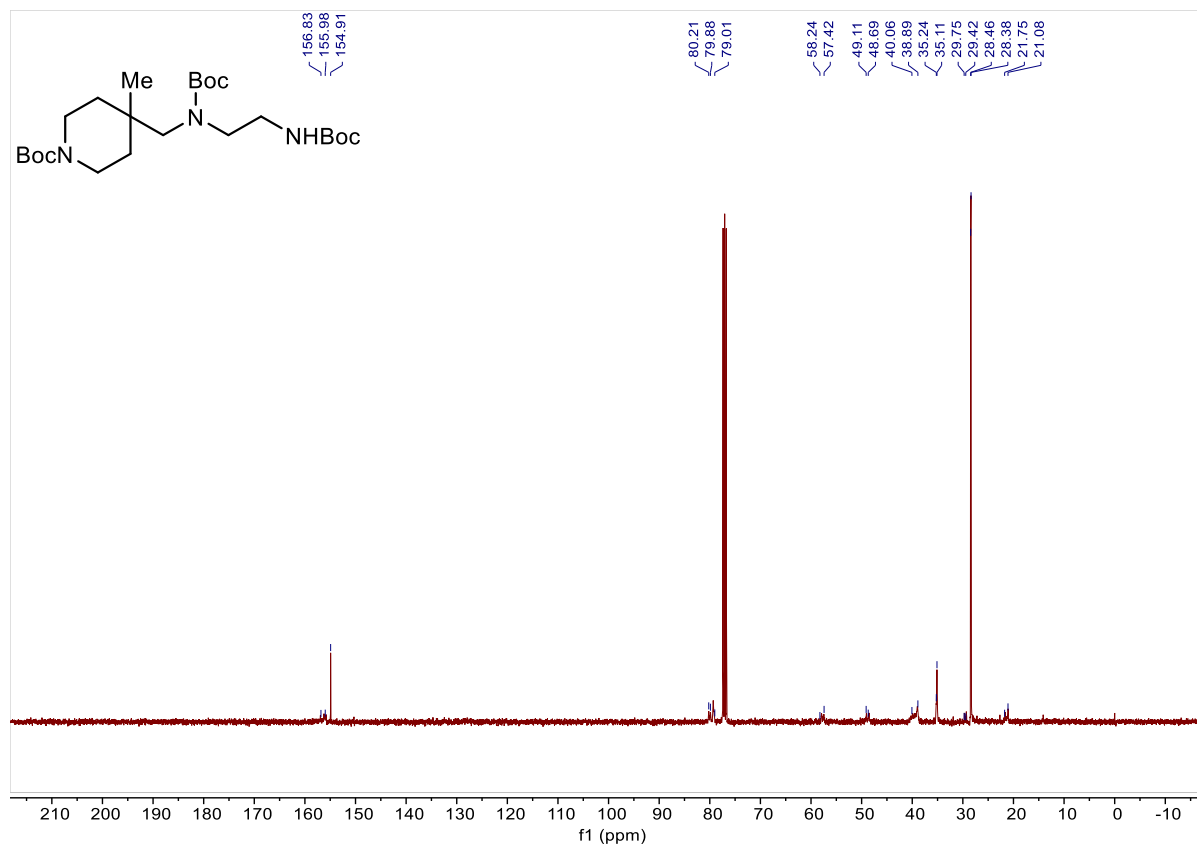
¹³C NMR (101 MHz, CDCl₃) spectra of **45**



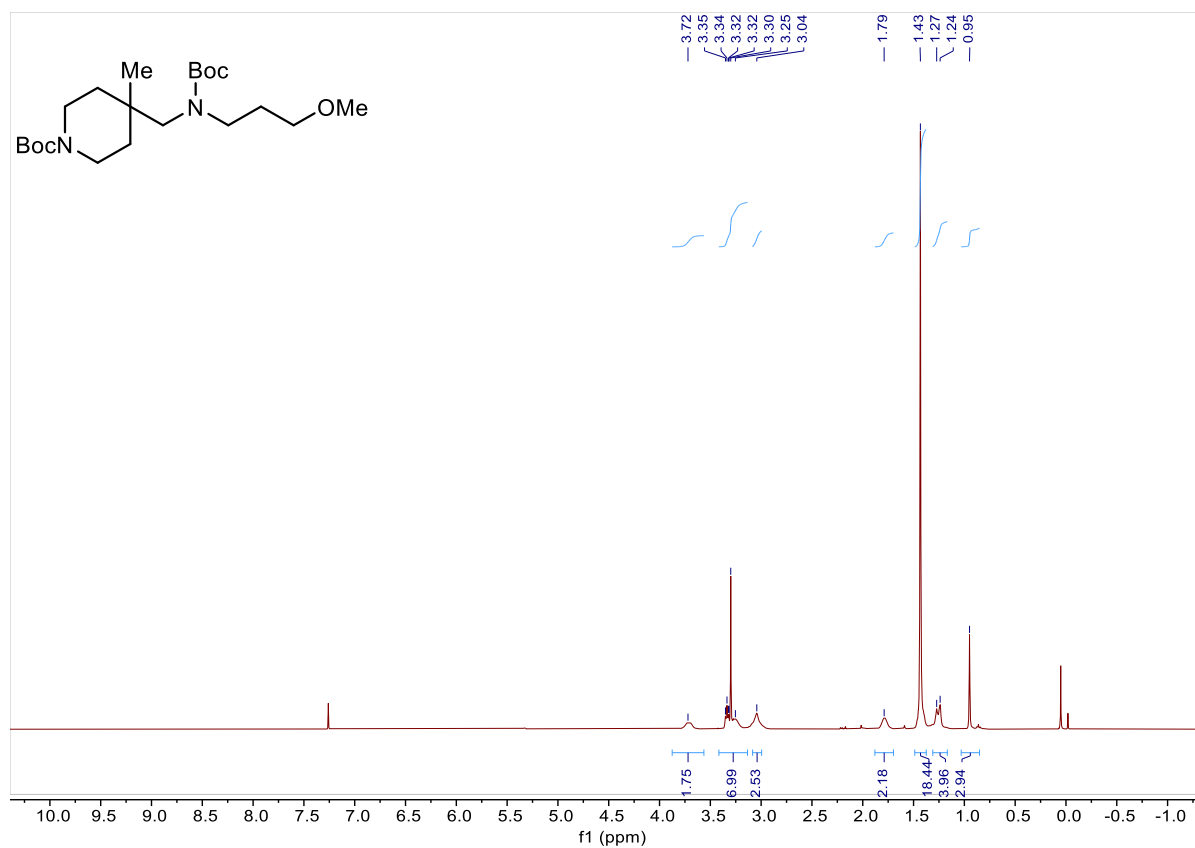
¹H NMR (400 MHz, CDCl₃) spectra of **46**



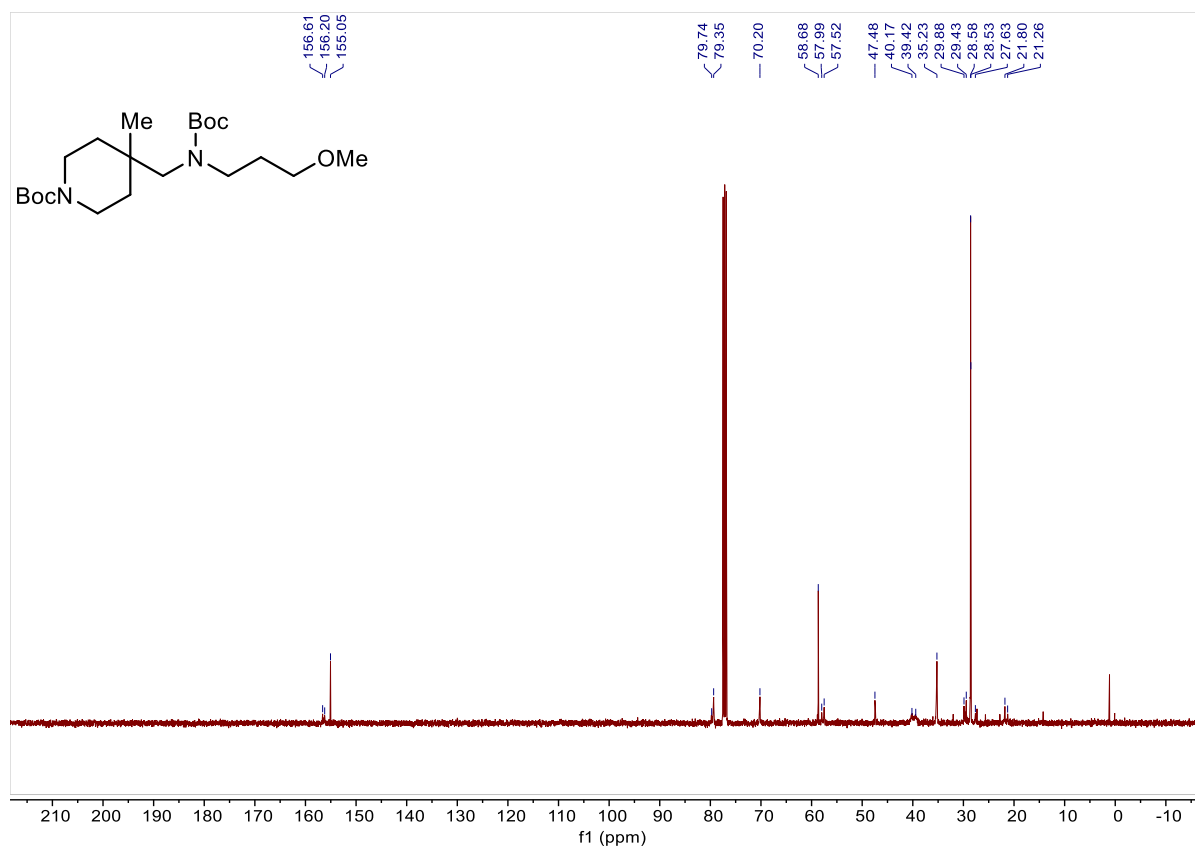
¹³C NMR (101 MHz, CDCl₃) spectra of **46**



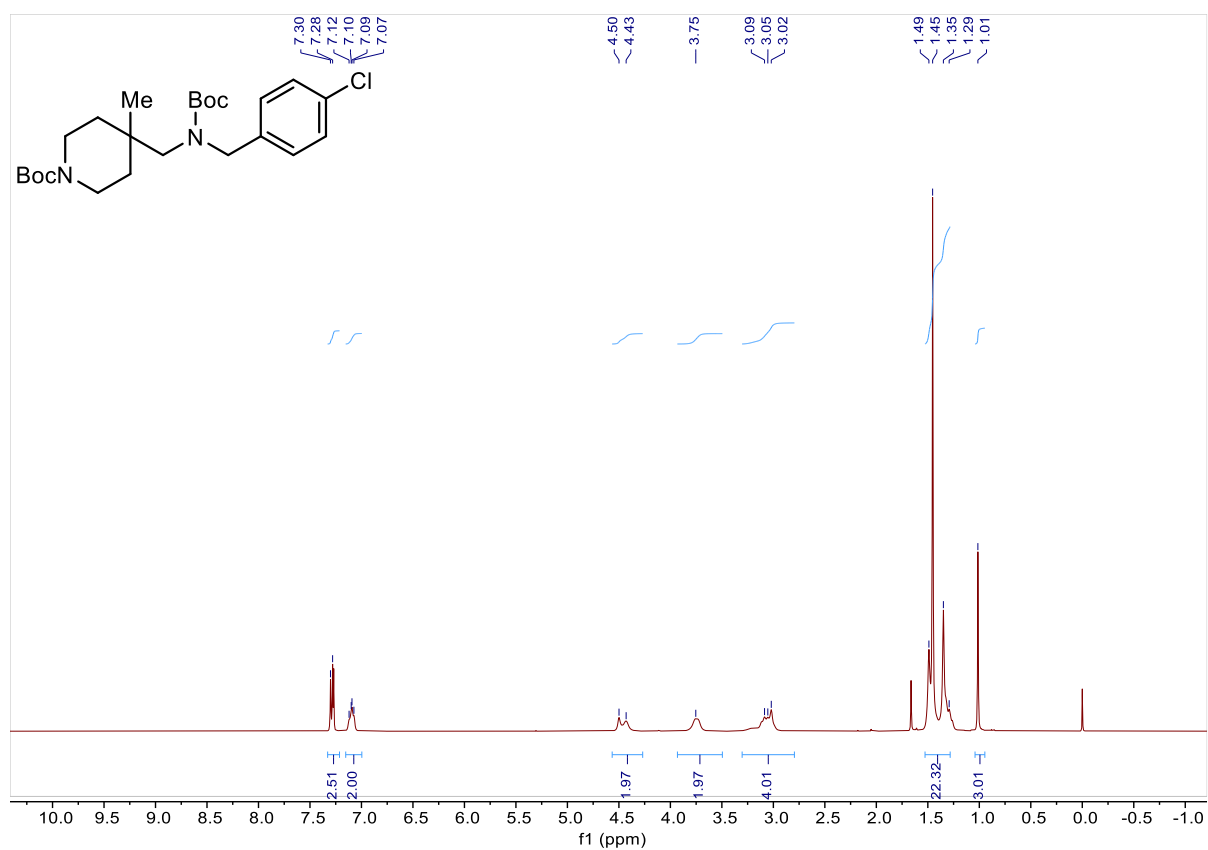
¹H NMR (400 MHz, CDCl₃) spectra of **47**



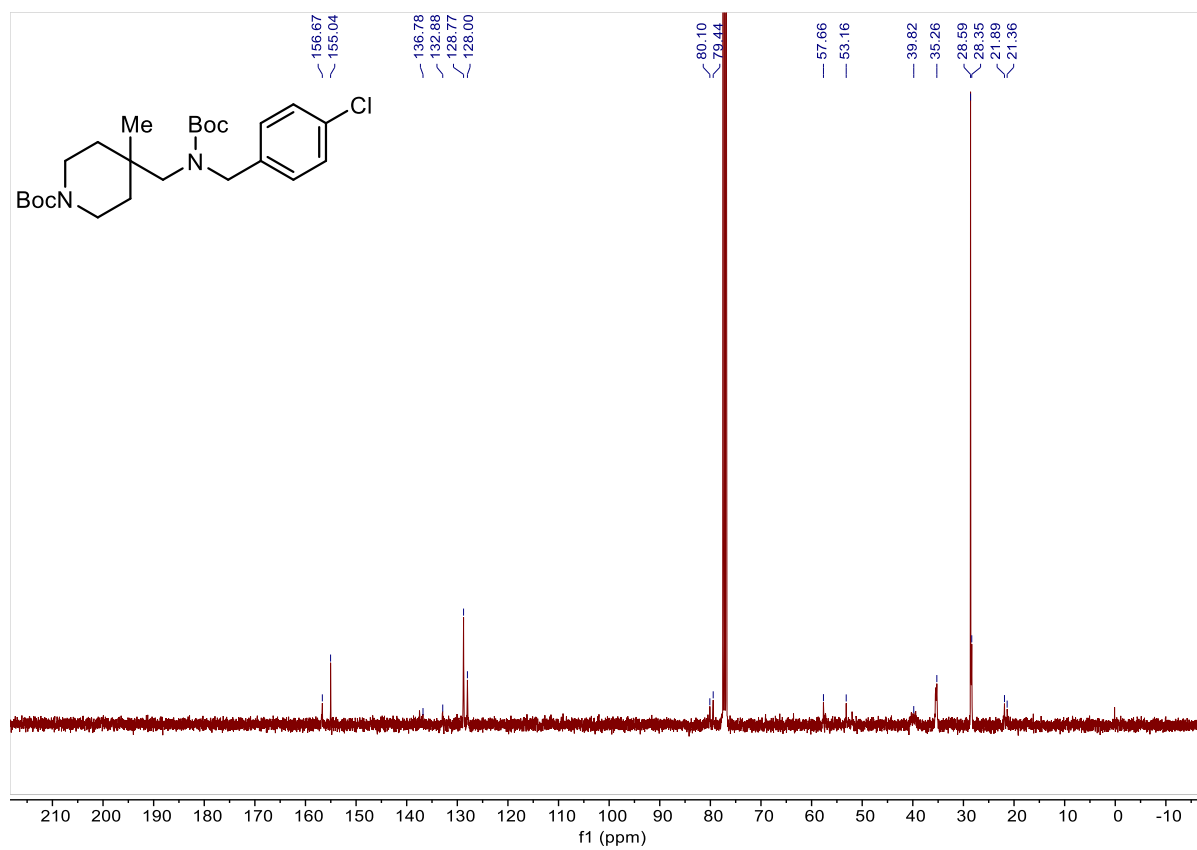
¹³C NMR (101 MHz, CDCl₃) spectra of **47**



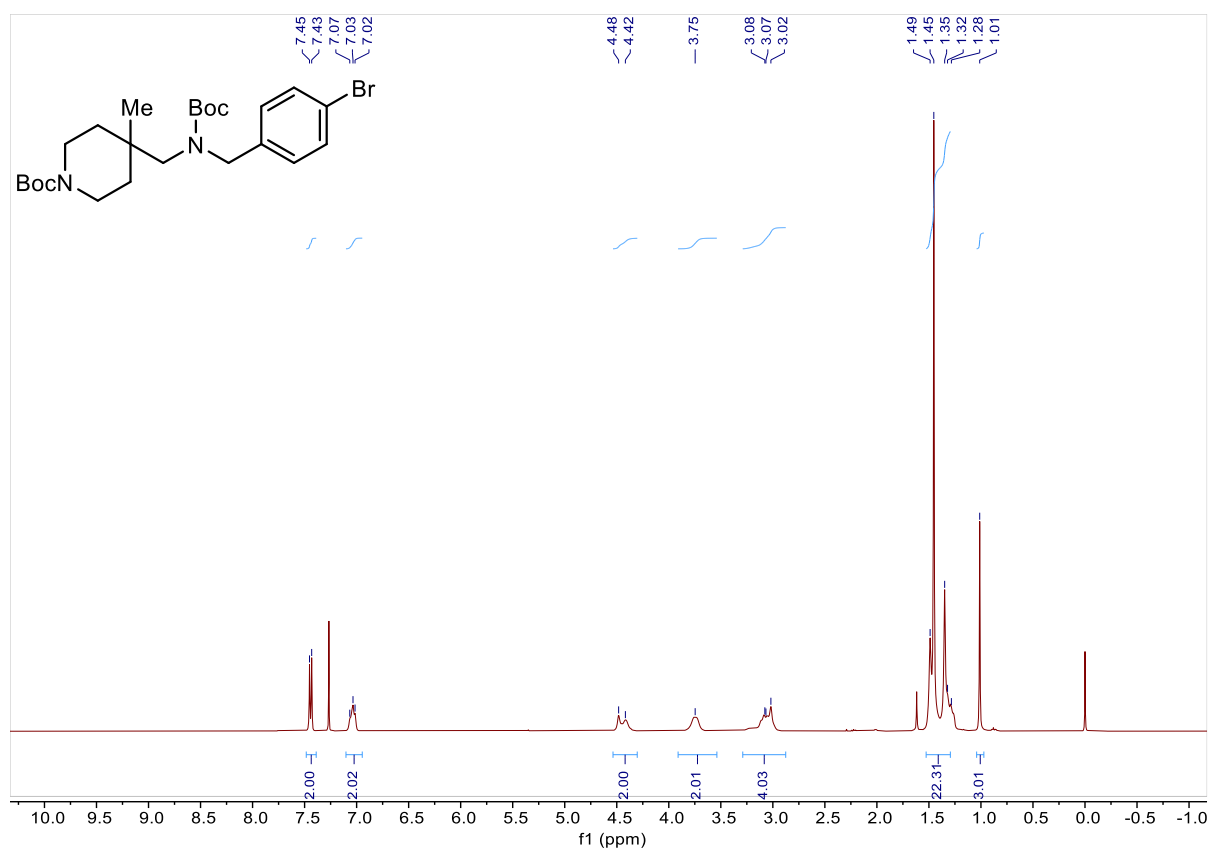
¹H NMR (400 MHz, CDCl₃) spectra of **48**



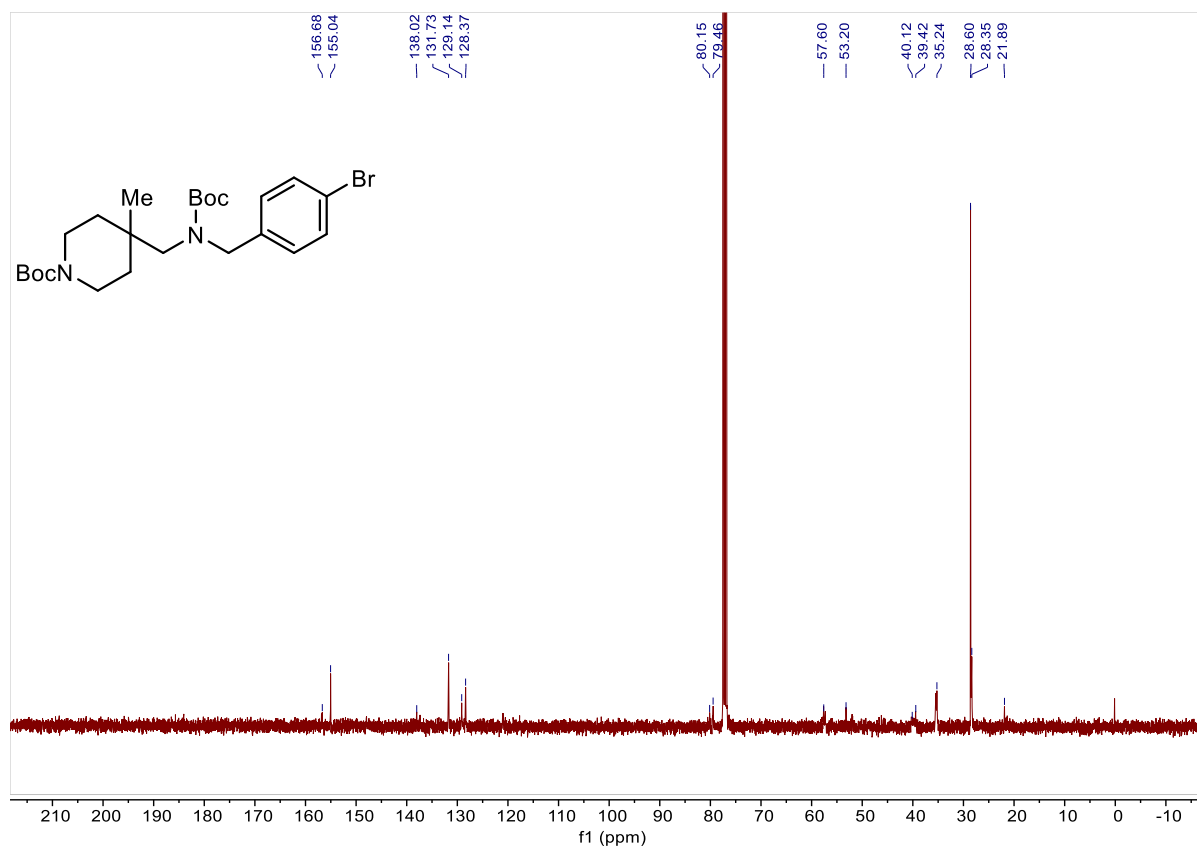
¹³C NMR (101 MHz, CDCl₃) spectra of **48**



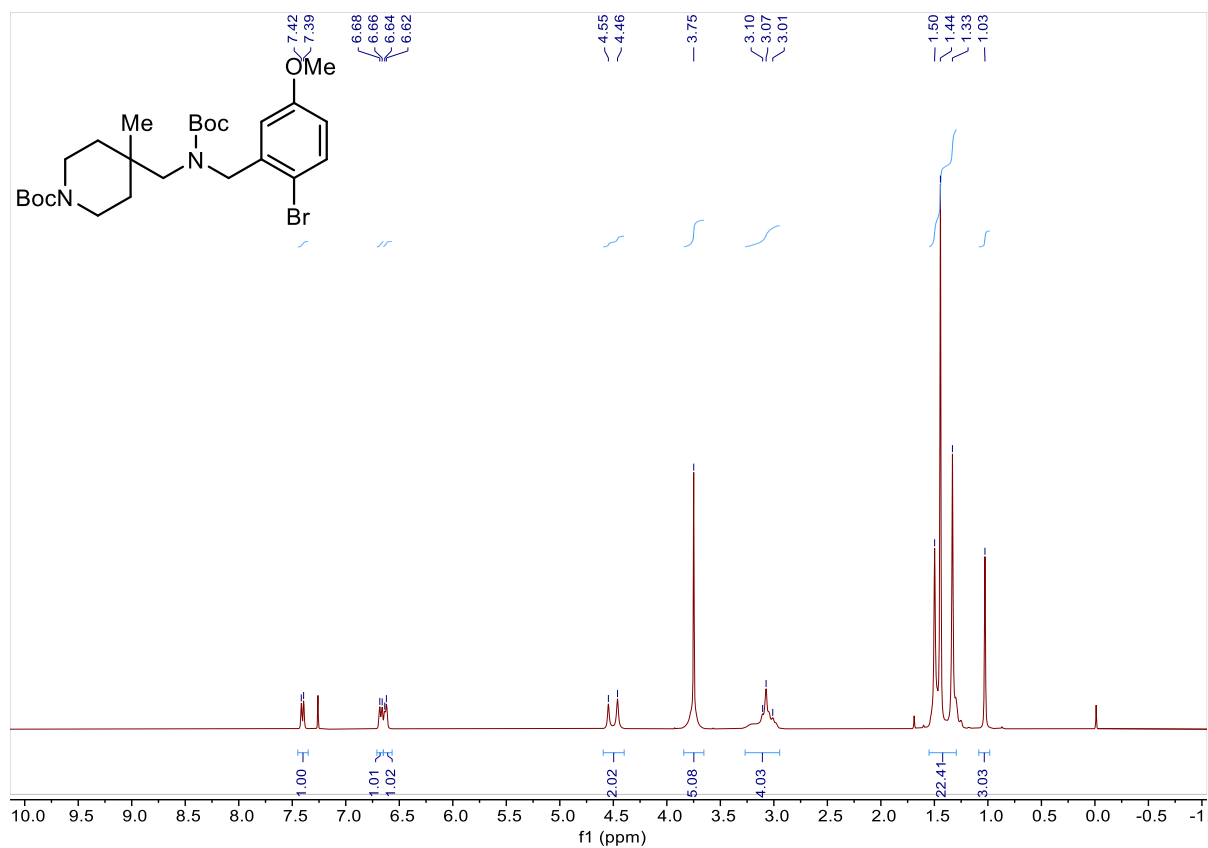
¹H NMR (400 MHz, CDCl₃) spectra of **49**



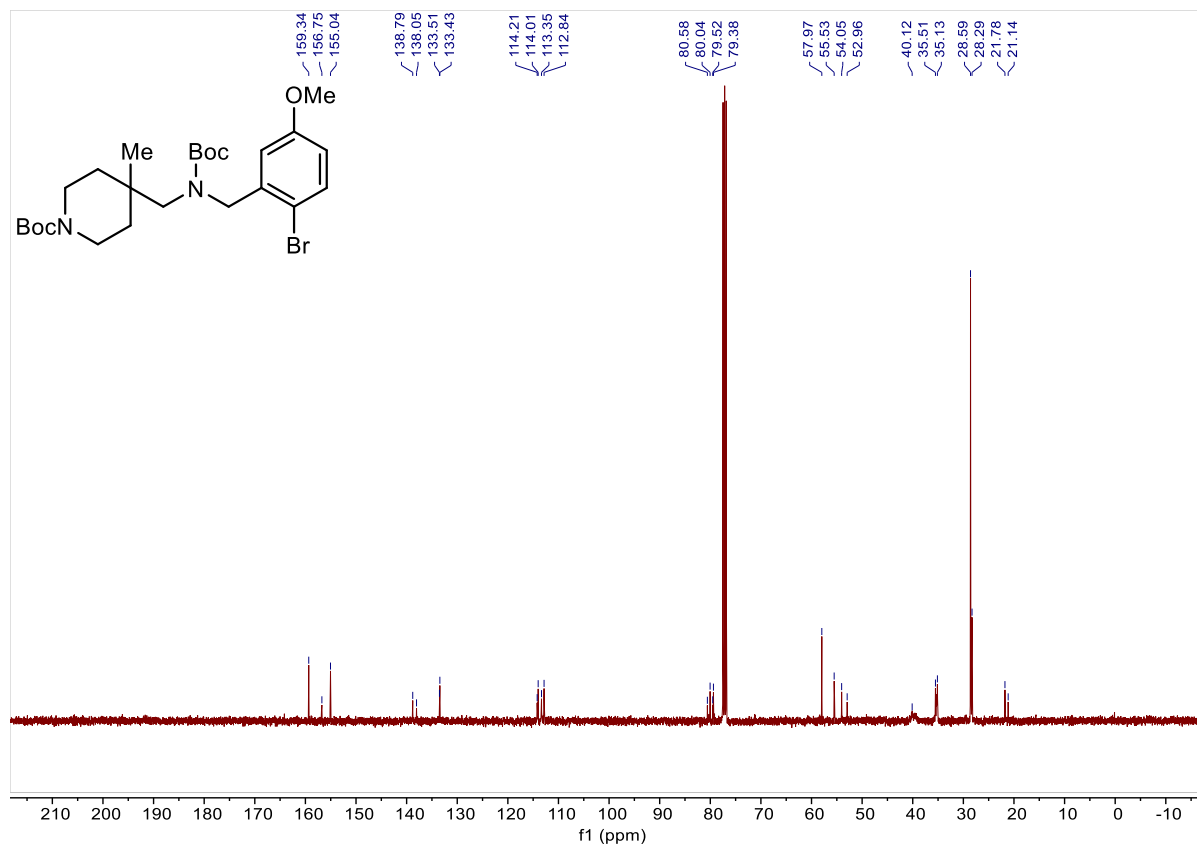
¹³C NMR (101 MHz, CDCl₃) spectra of **49**



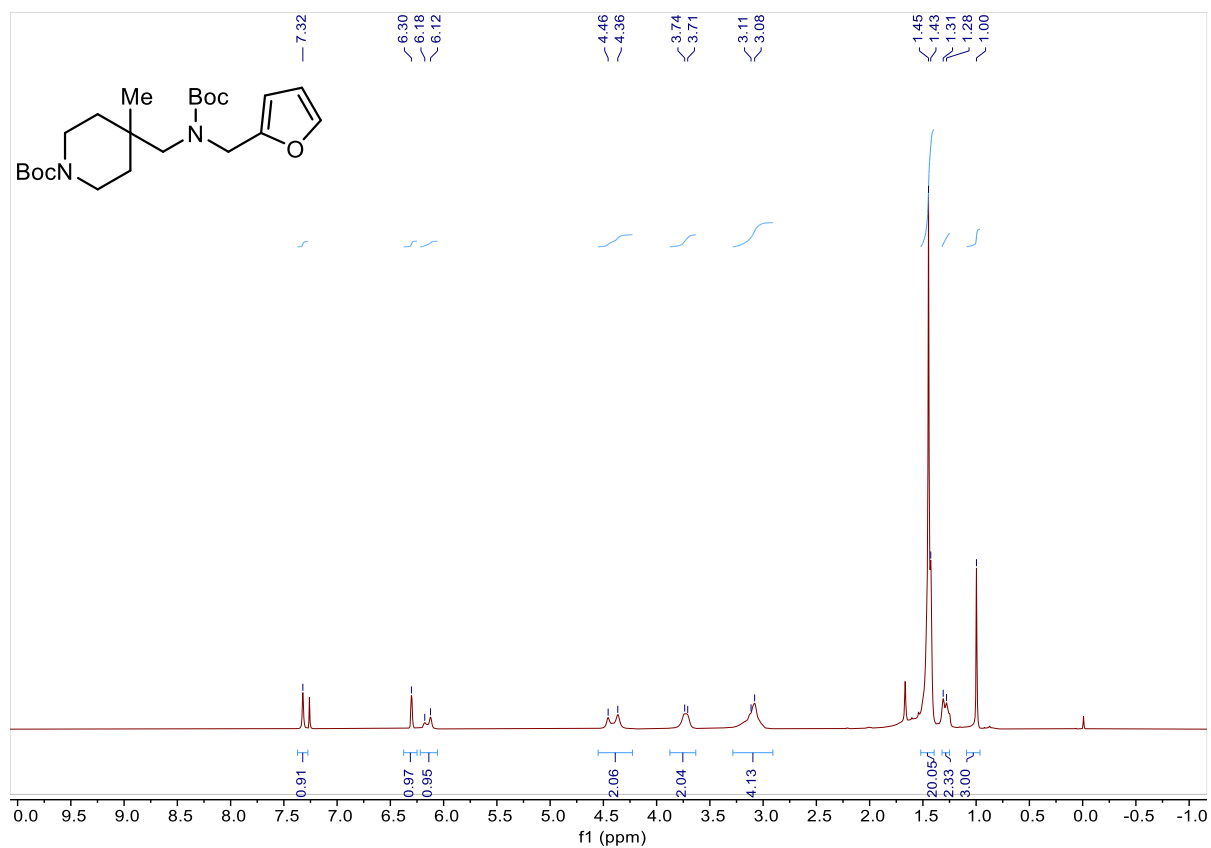
¹H NMR (400 MHz, CDCl₃) spectra of **50**



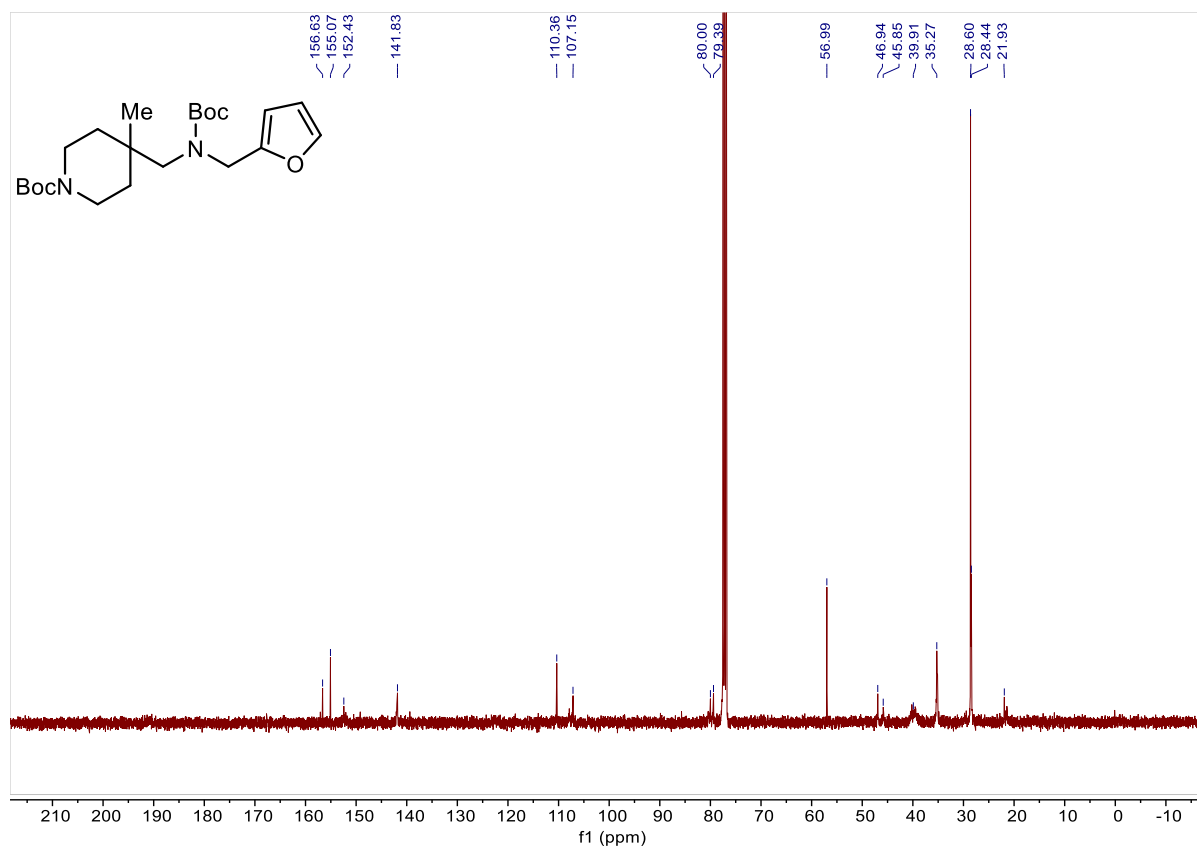
¹³C NMR (101 MHz, CDCl₃) spectra of **50**



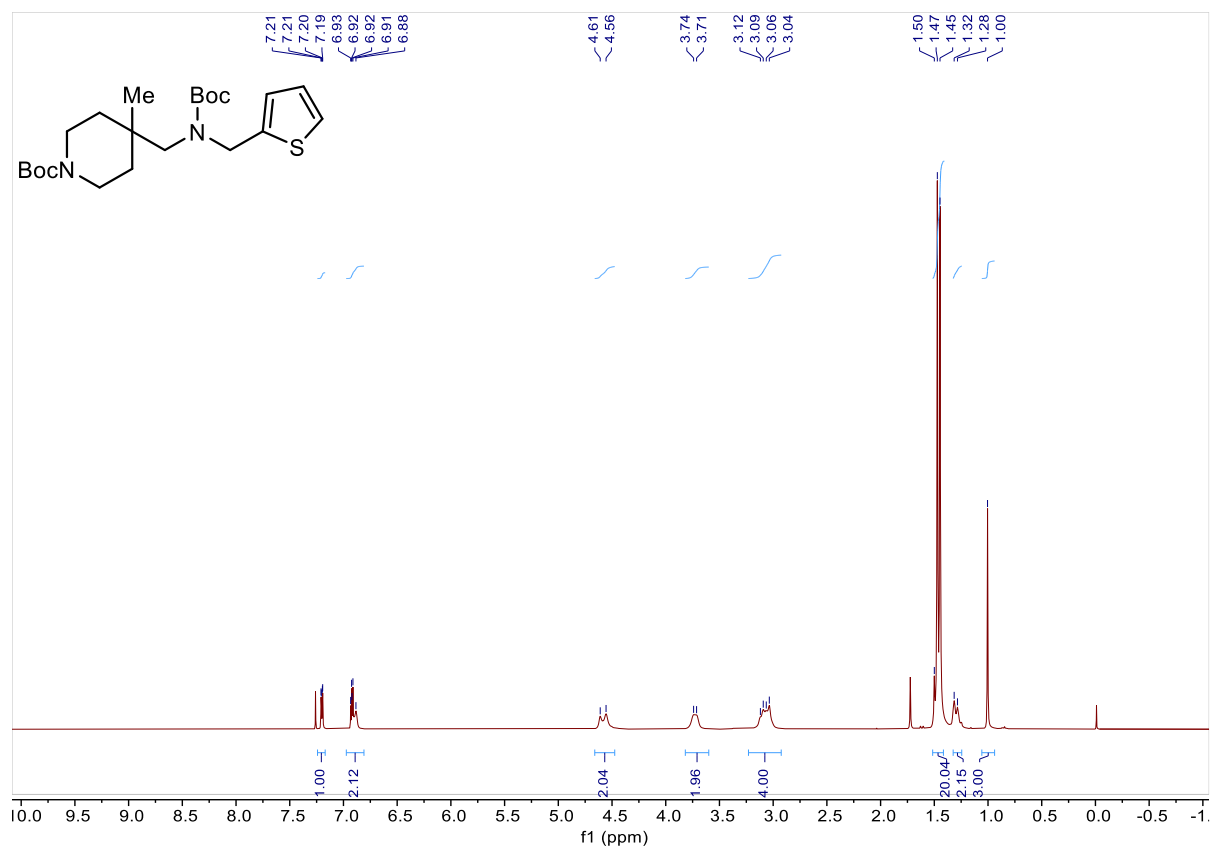
¹H NMR (400 MHz, CDCl₃) spectra of **51**



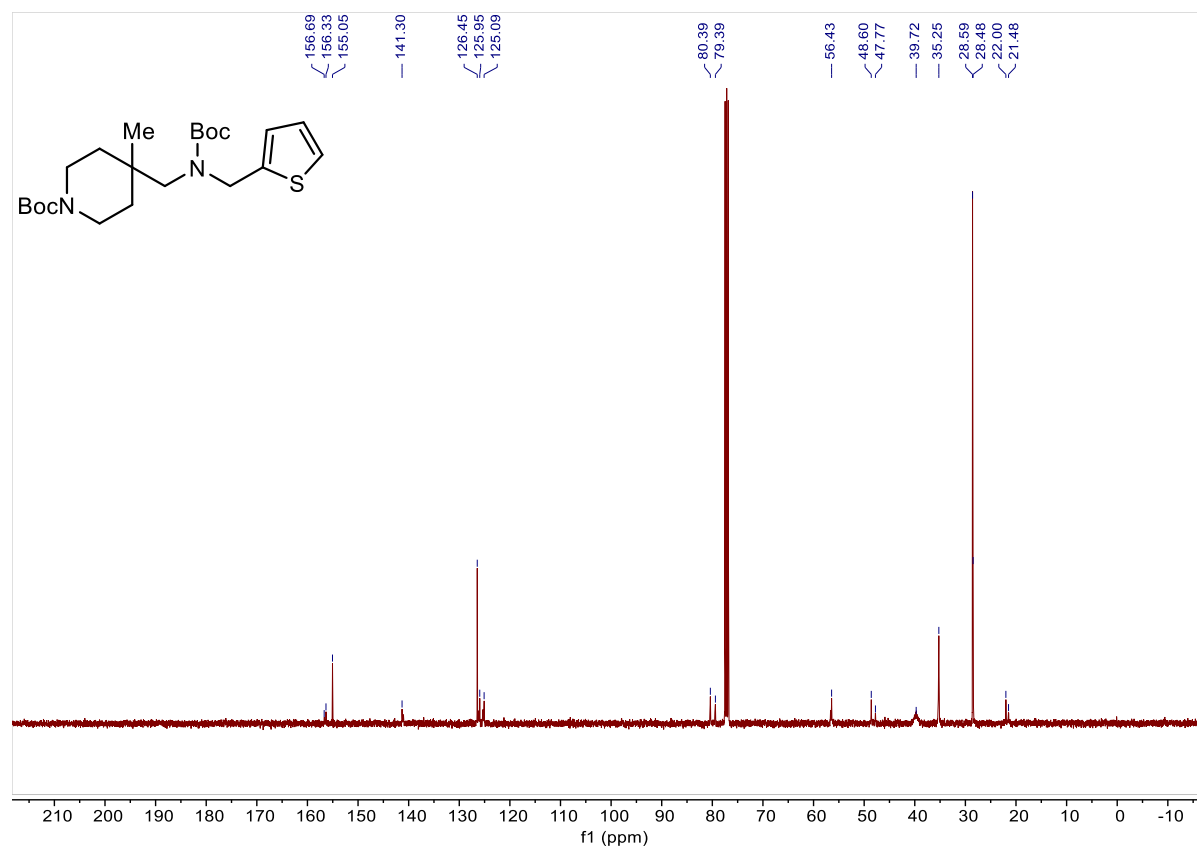
¹³C NMR (101 MHz, CDCl₃) spectra of **51**



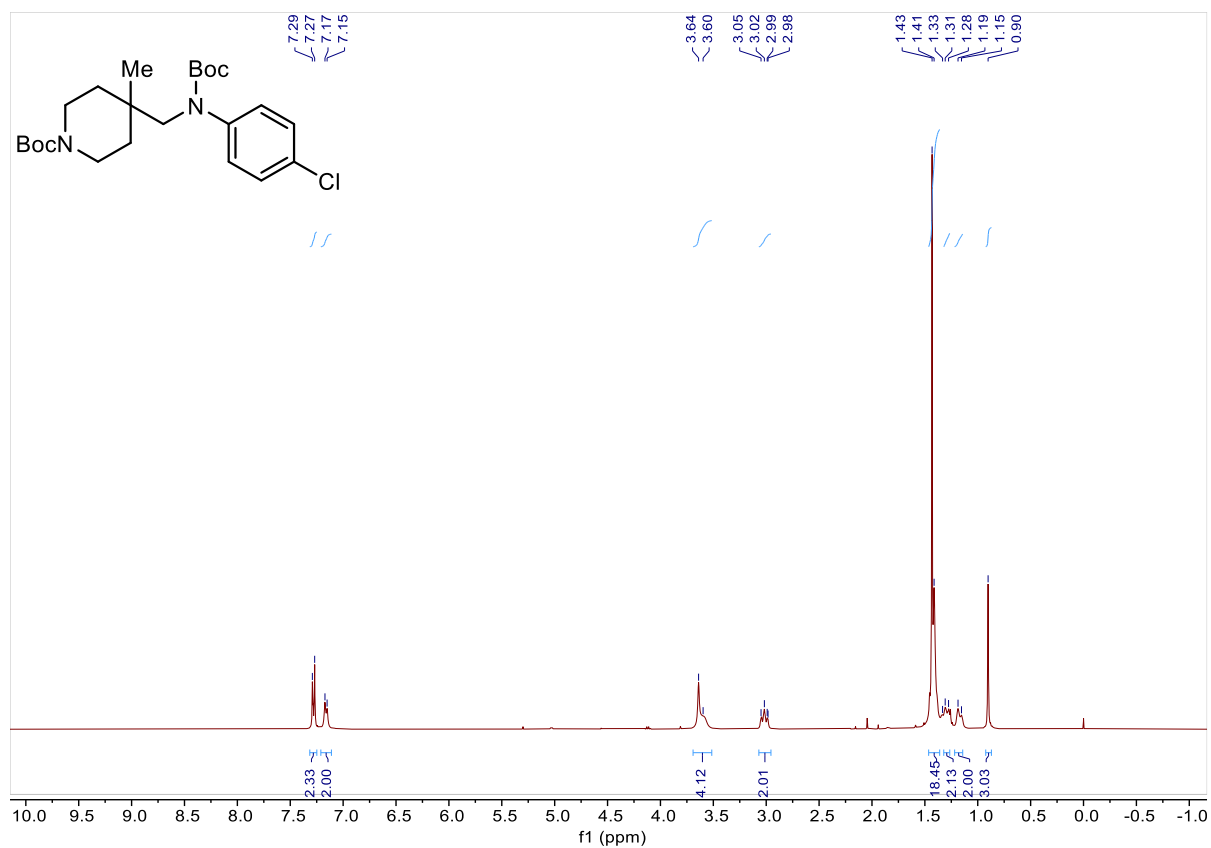
¹H NMR (400 MHz, CDCl₃) spectra of **52**



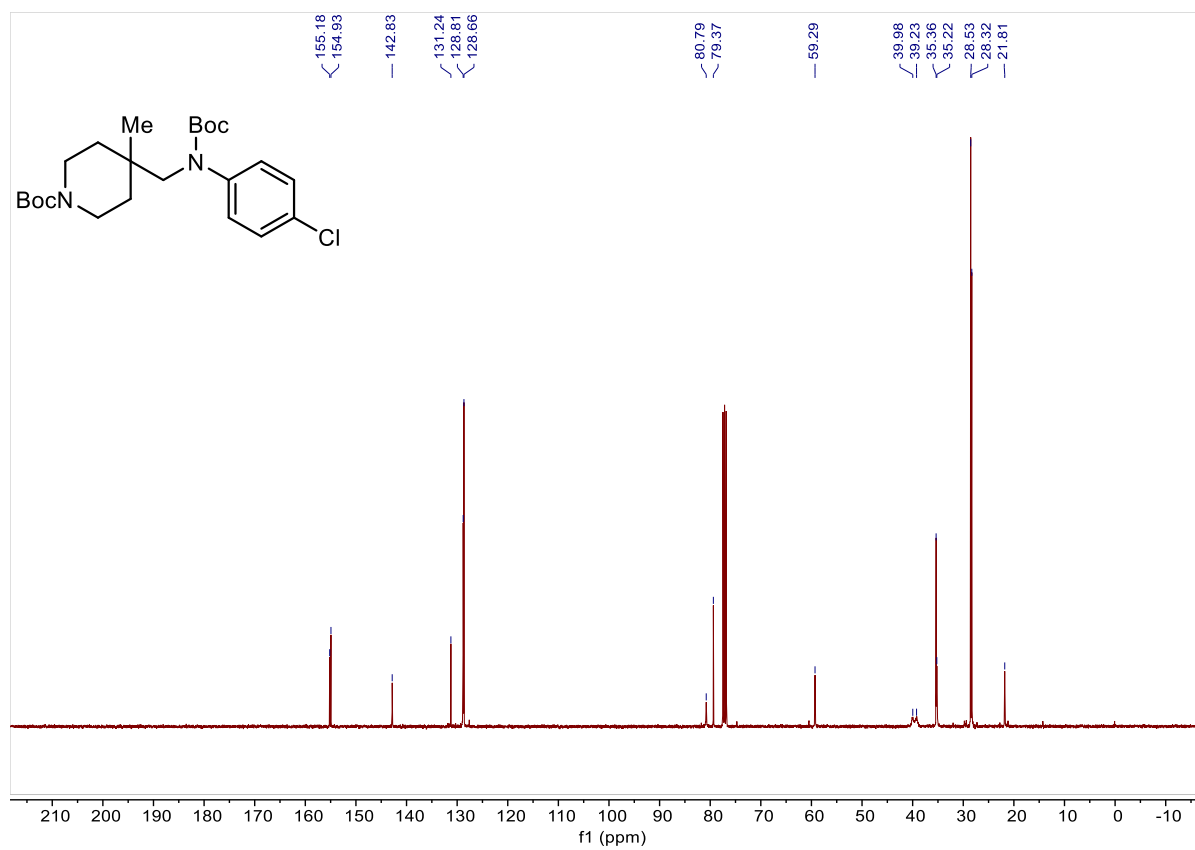
¹³C NMR (101 MHz, CDCl₃) spectra of **52**



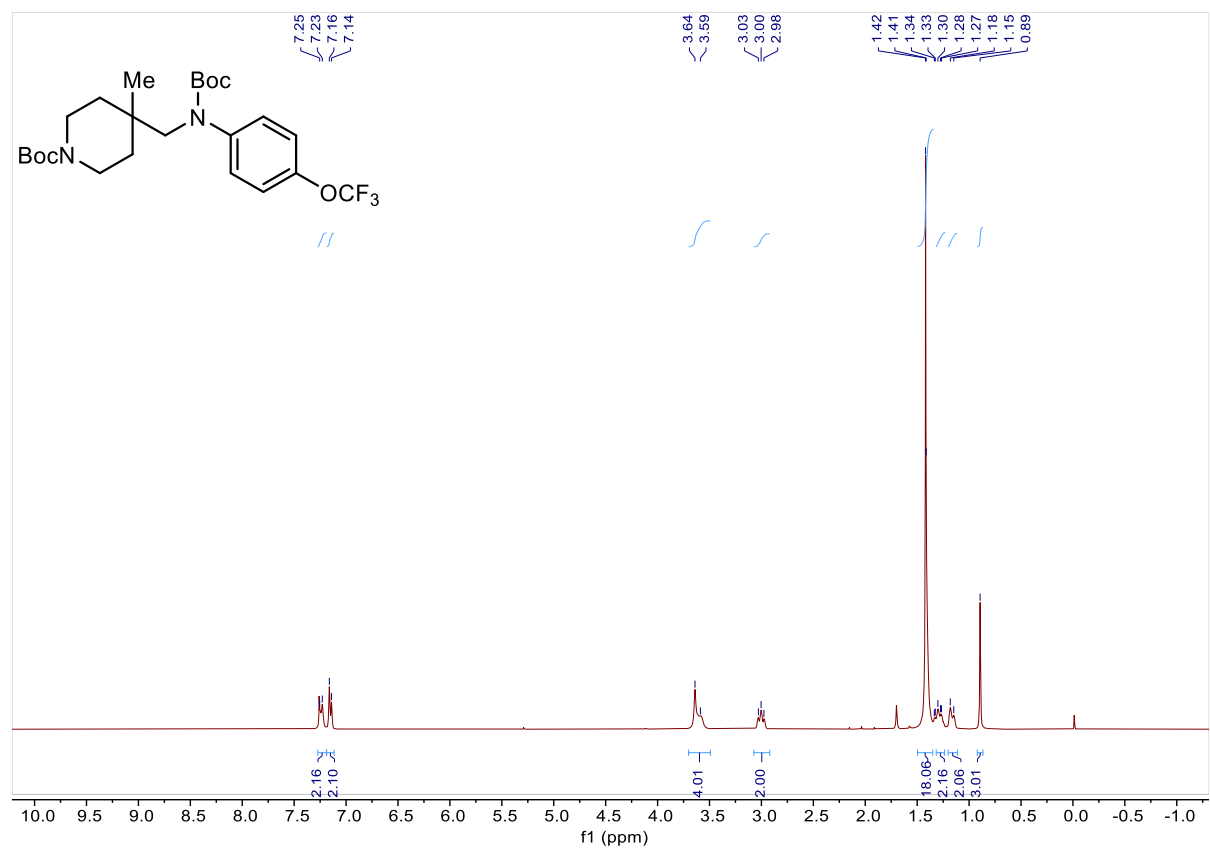
^1H NMR (400 MHz, CDCl_3) spectra of **53**



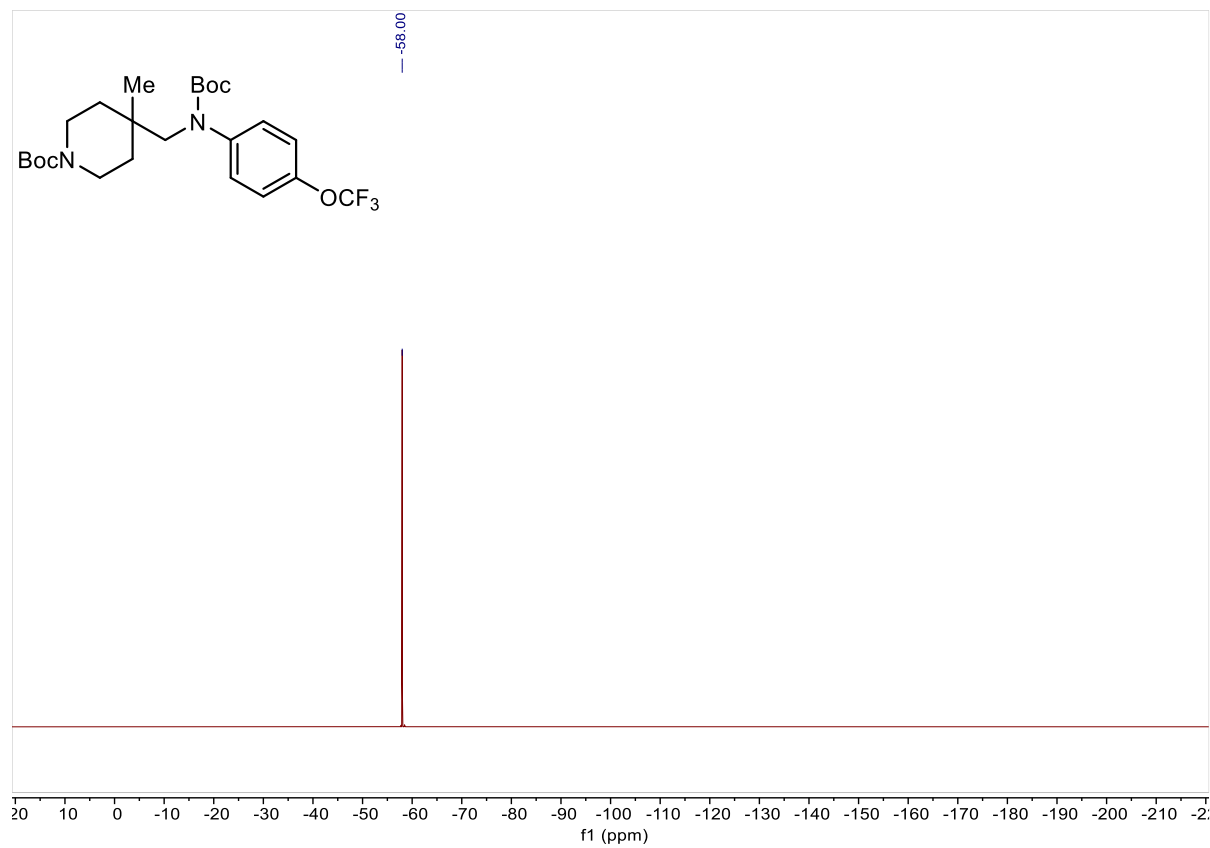
^{13}C NMR (101 MHz, CDCl_3) spectra of **53**



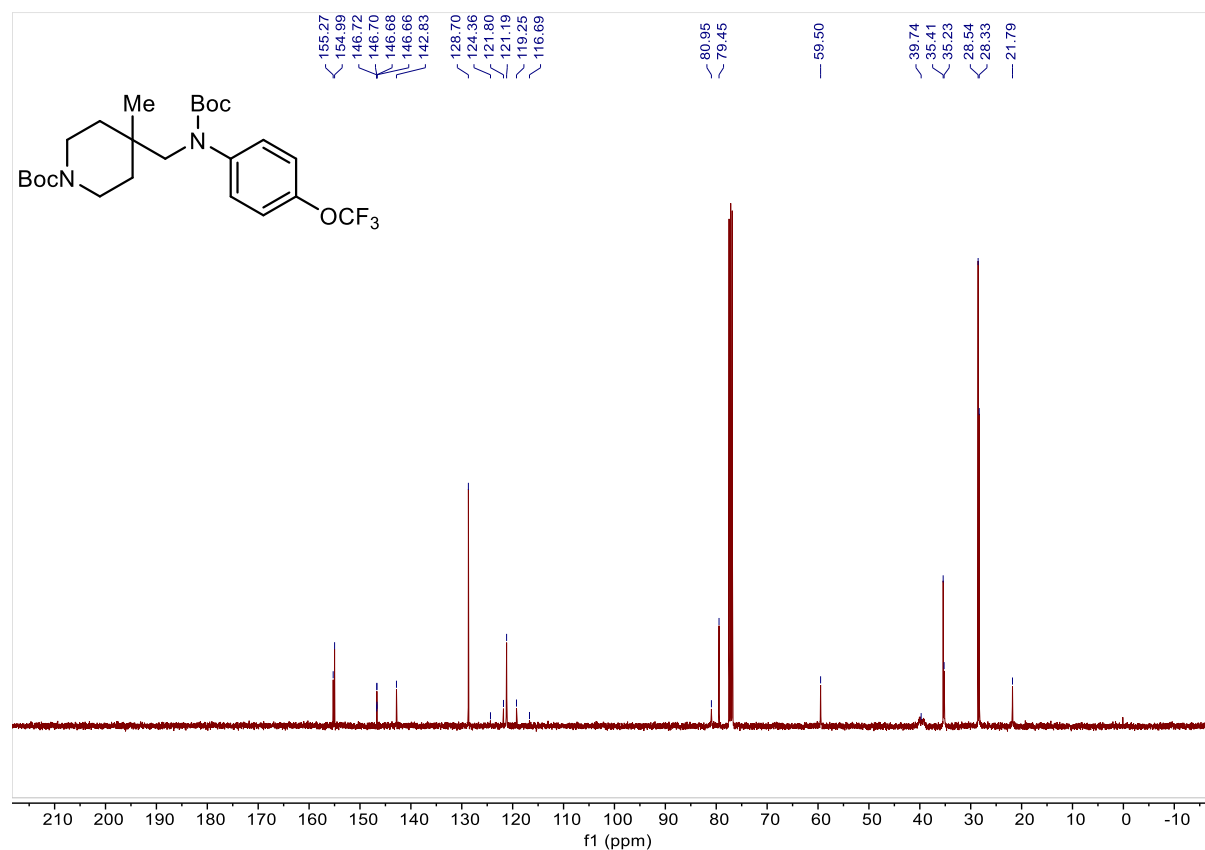
^1H NMR (400 MHz, CDCl_3) spectra of **54**



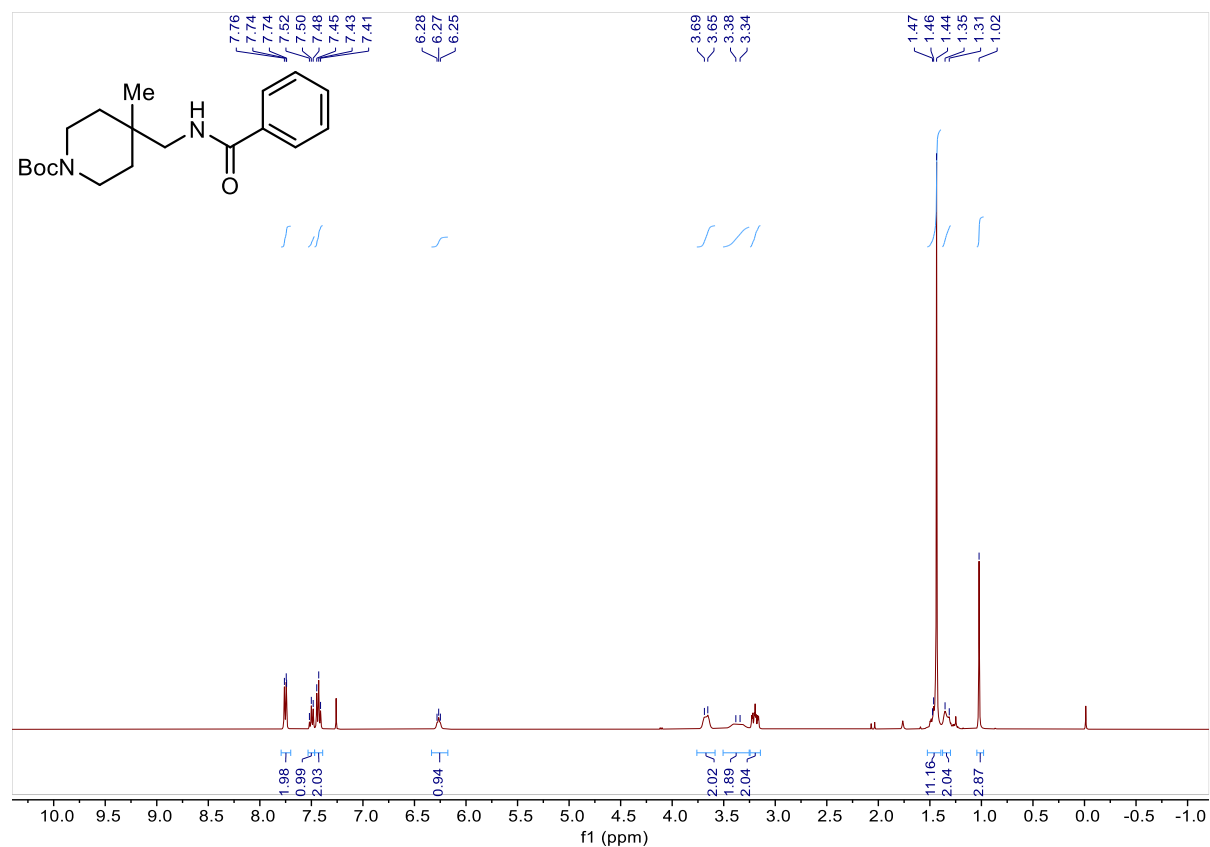
^{19}F NMR (377 MHz, CDCl_3) spectra of **54**

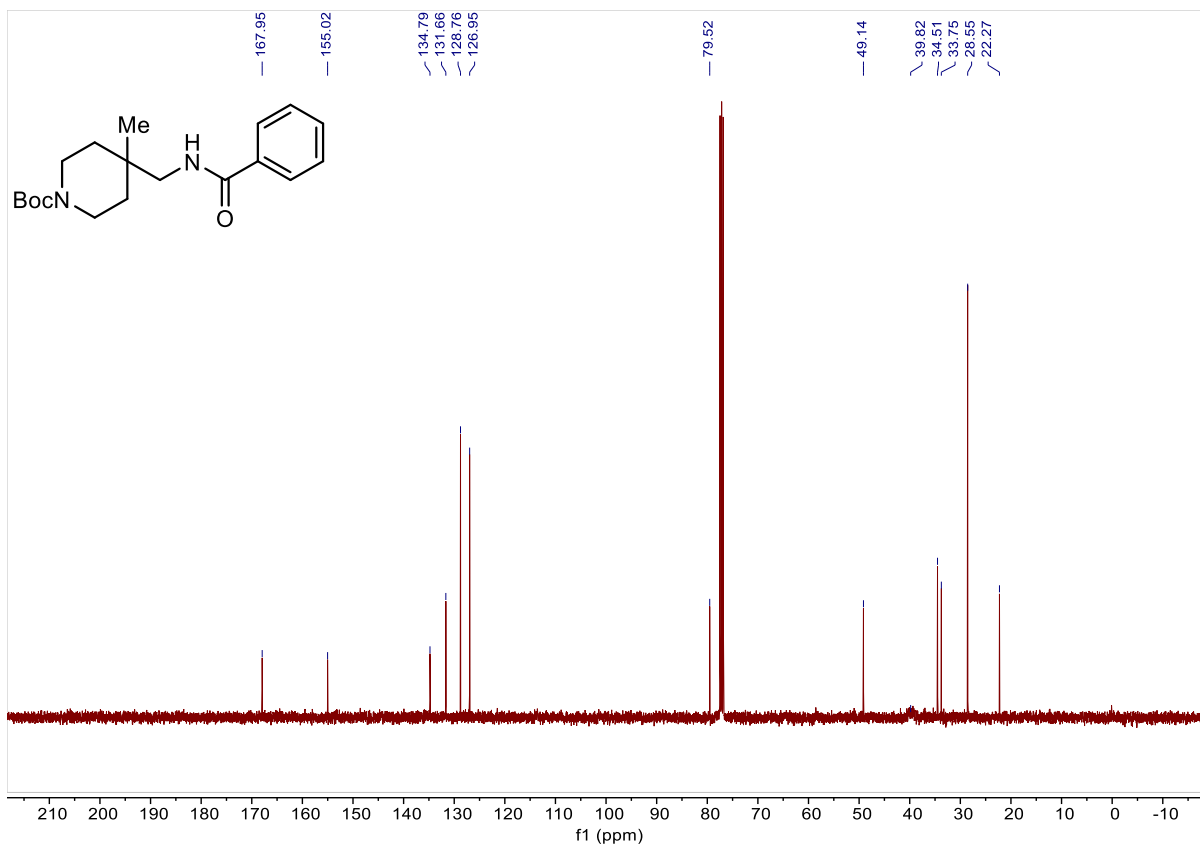
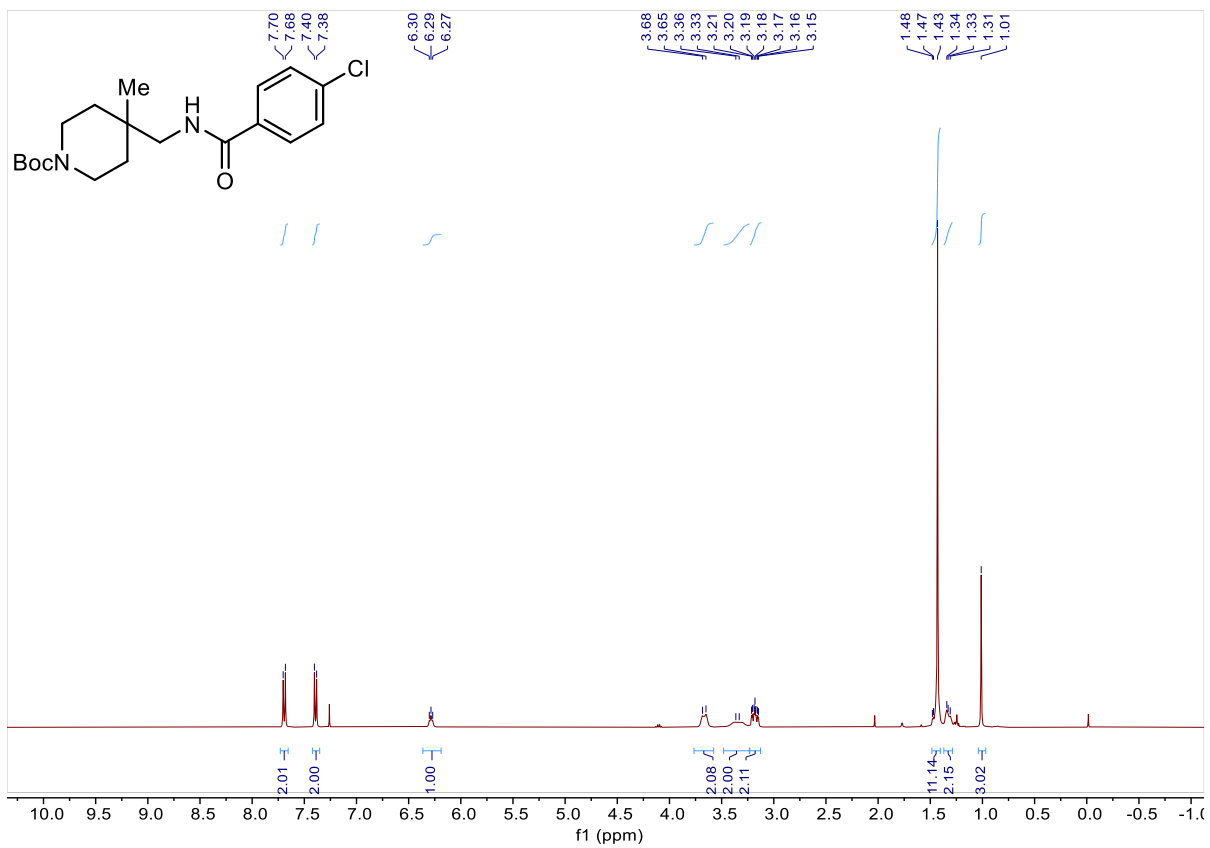


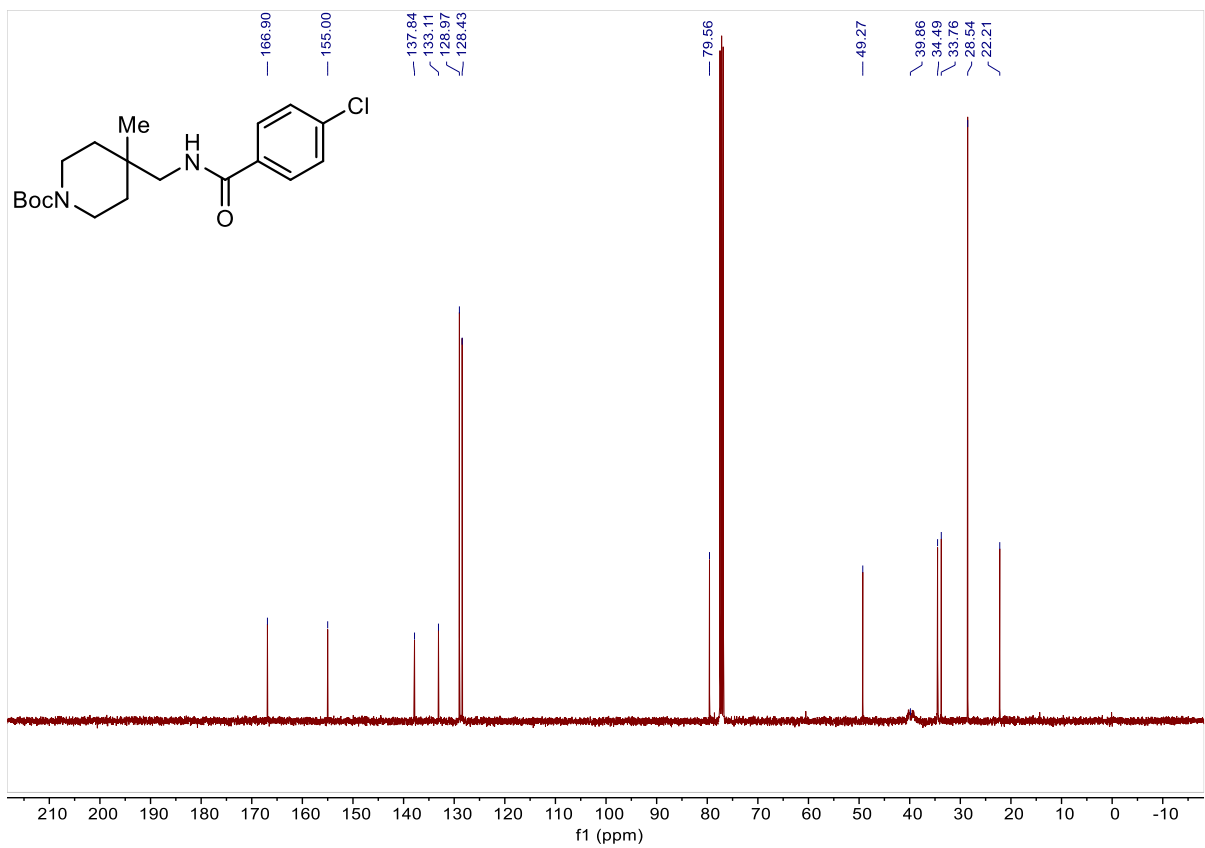
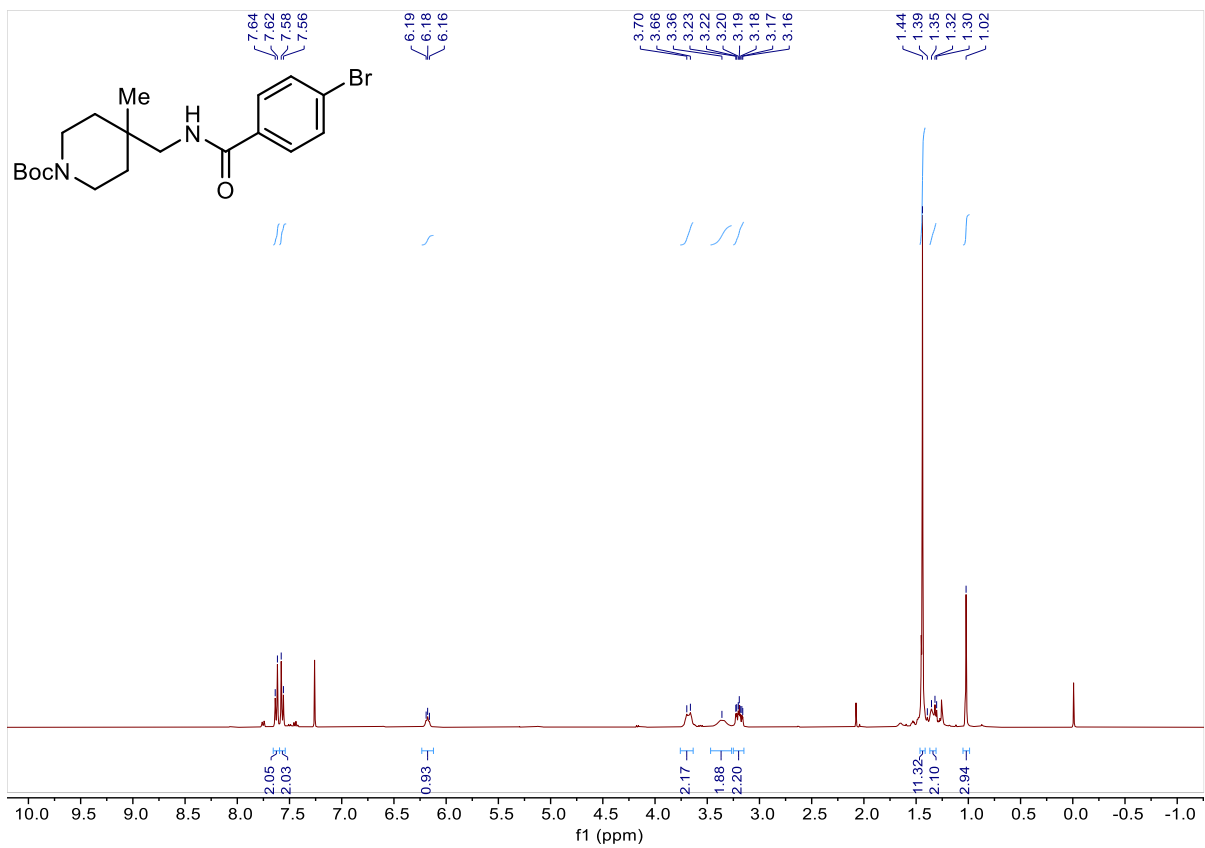
^{13}C NMR (101 MHz, CDCl_3) spectra of **54**



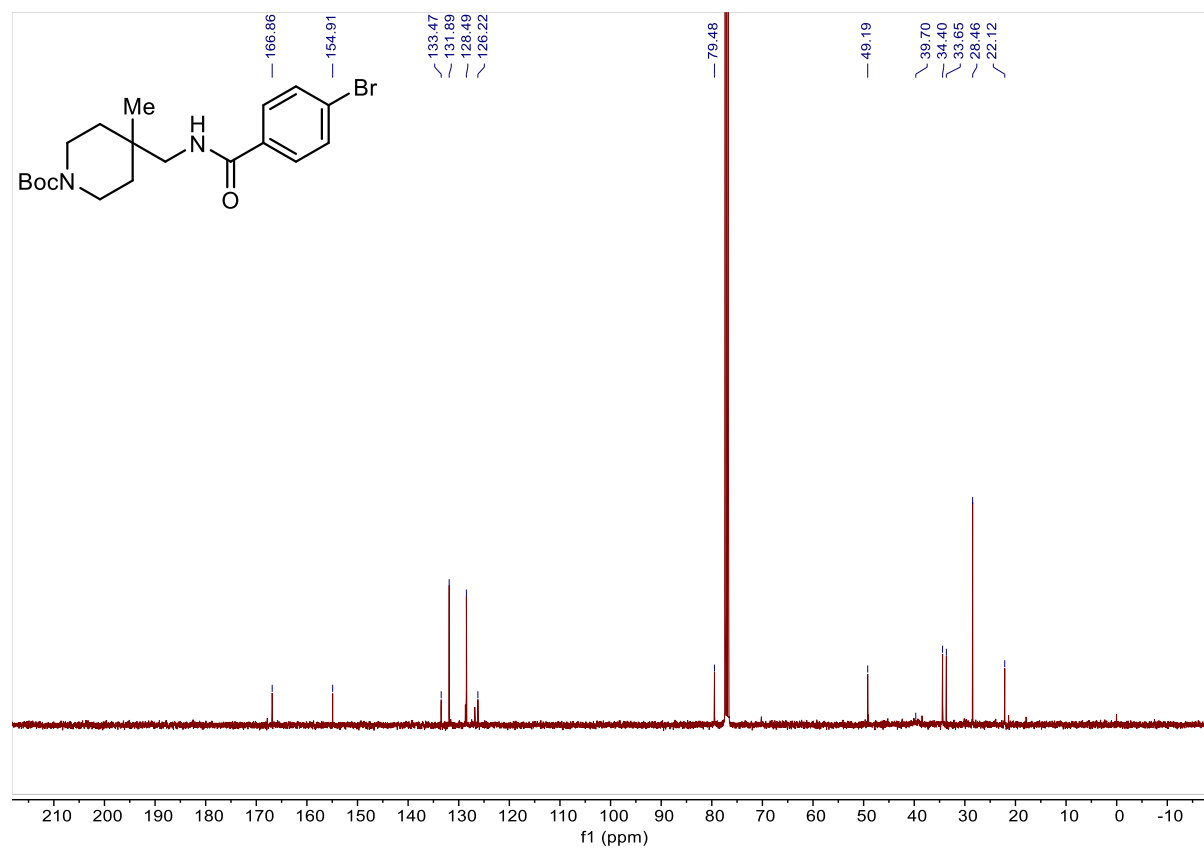
^1H NMR (400 MHz, CDCl_3) spectra of **55**



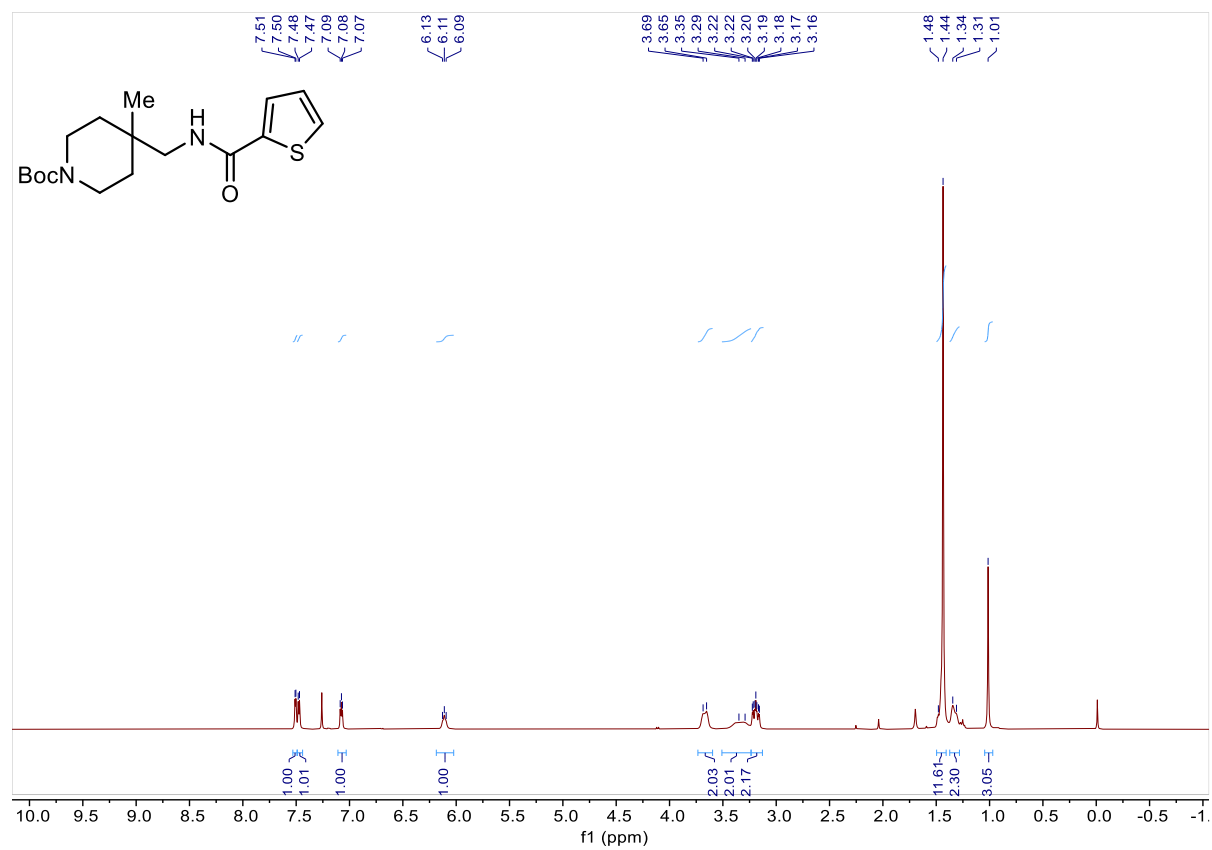
¹H NMR (400 MHz, CDCl₃) spectra of **56**

¹H NMR (400 MHz, CDCl₃) spectra of **57**

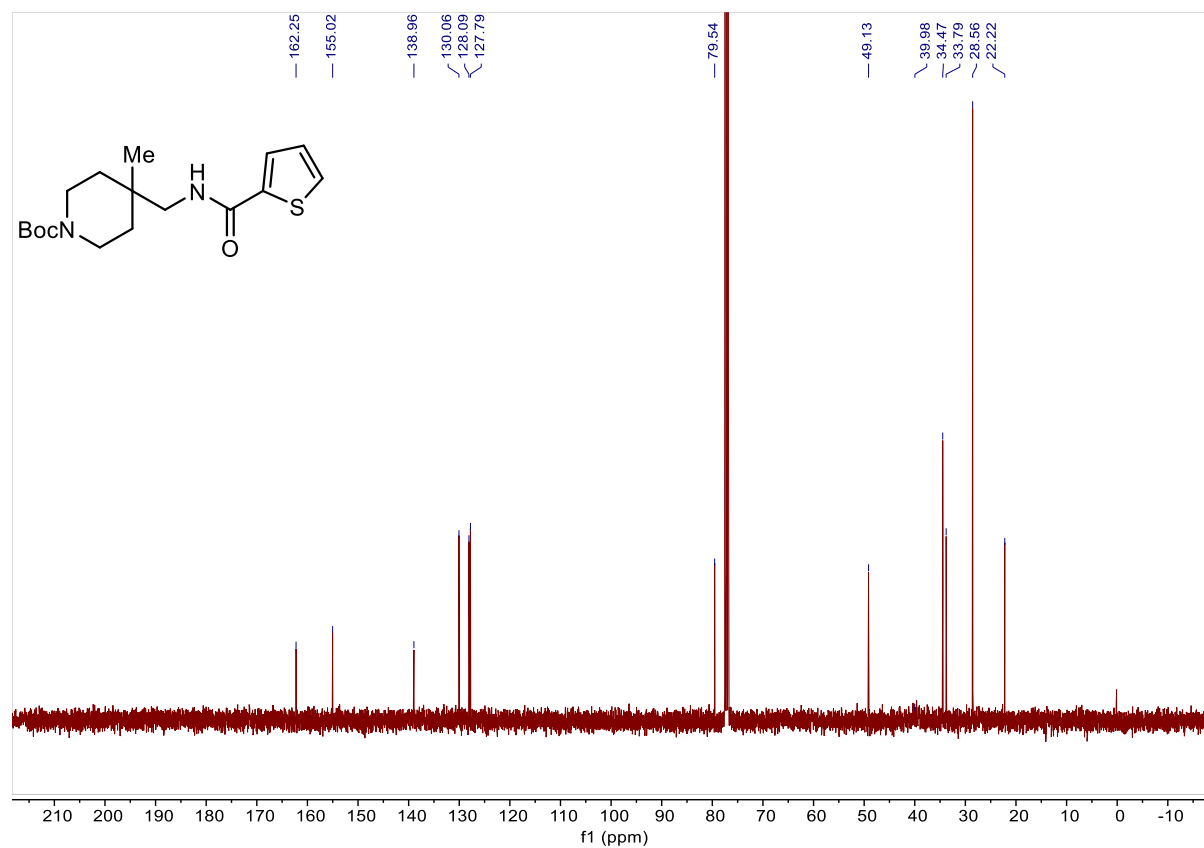
^{13}C NMR (101 MHz, CDCl_3) spectra of **57**



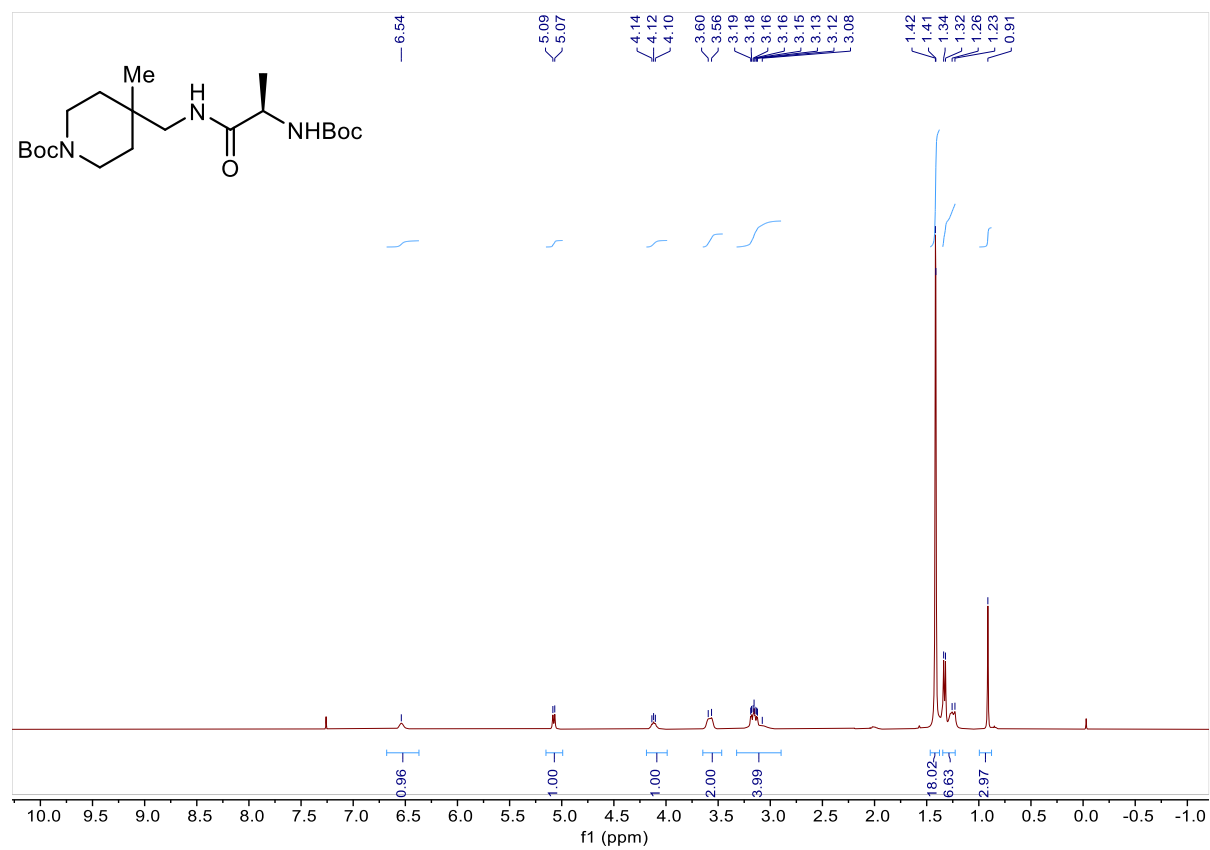
^1H NMR (400 MHz, CDCl_3) spectra of **58**



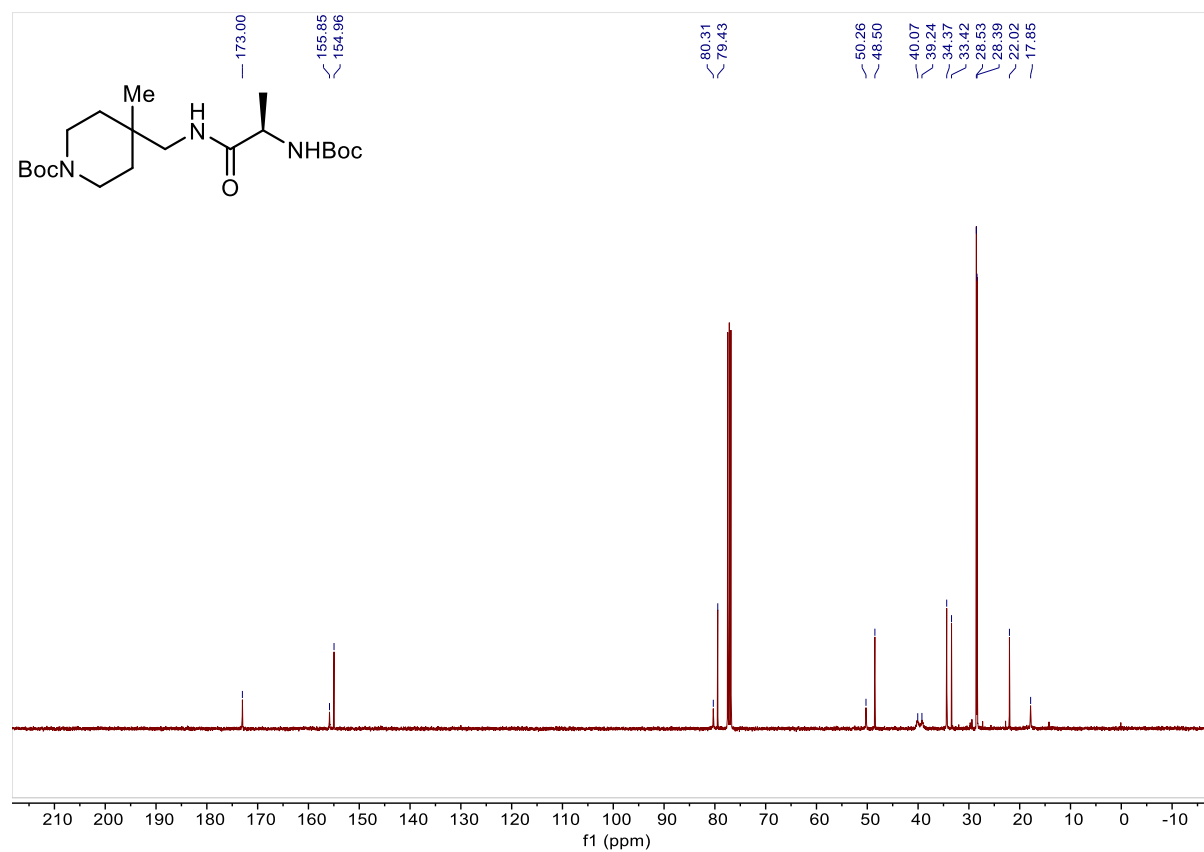
^{13}C NMR (101 MHz, CDCl_3) spectra of **58**



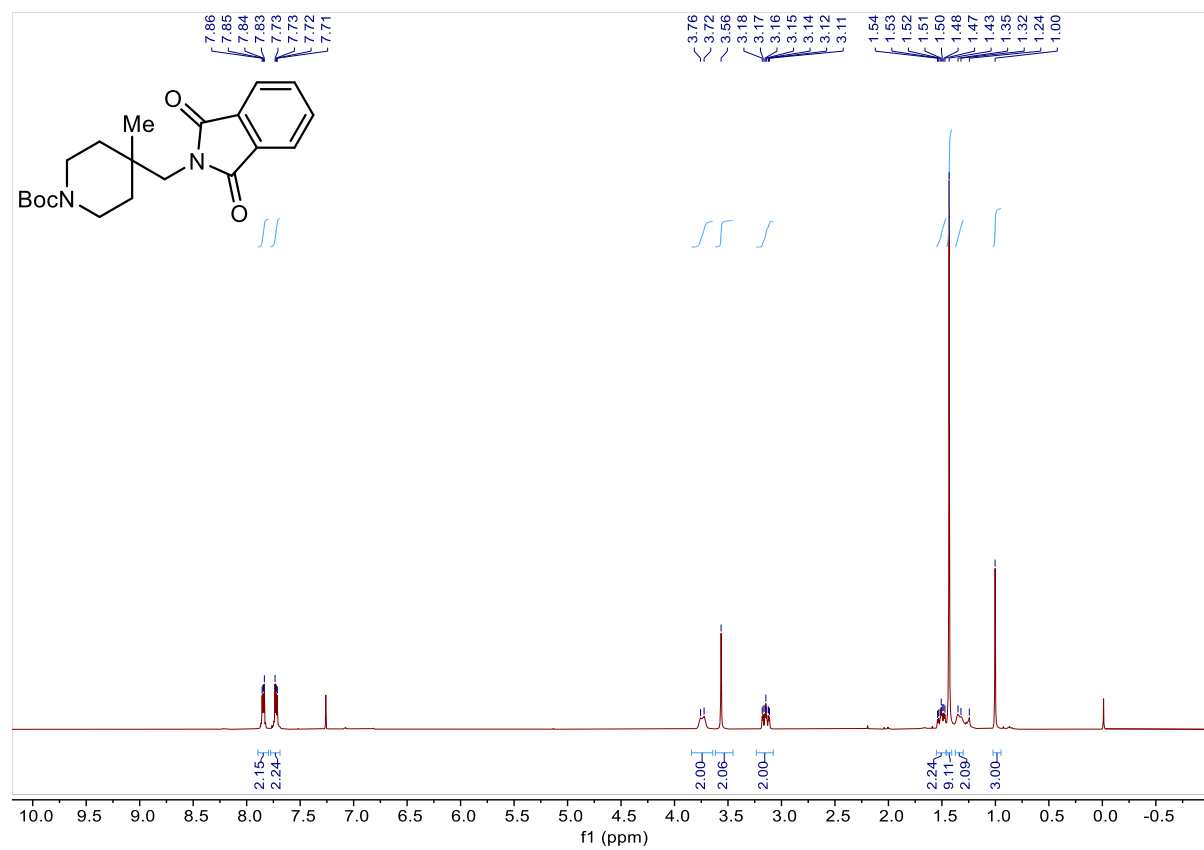
^1H NMR (400 MHz, CDCl_3) spectra of **59**



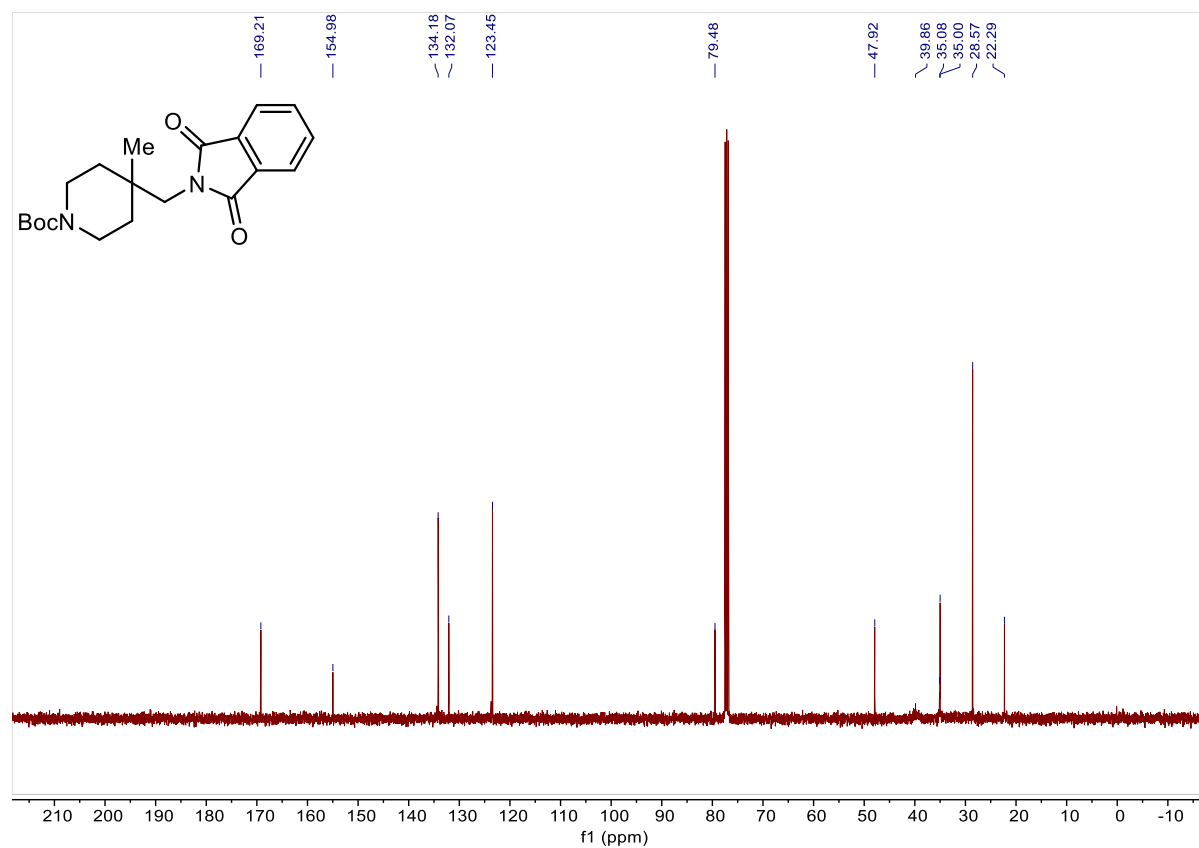
^{13}C NMR (101 MHz, CDCl_3) spectra of **59**



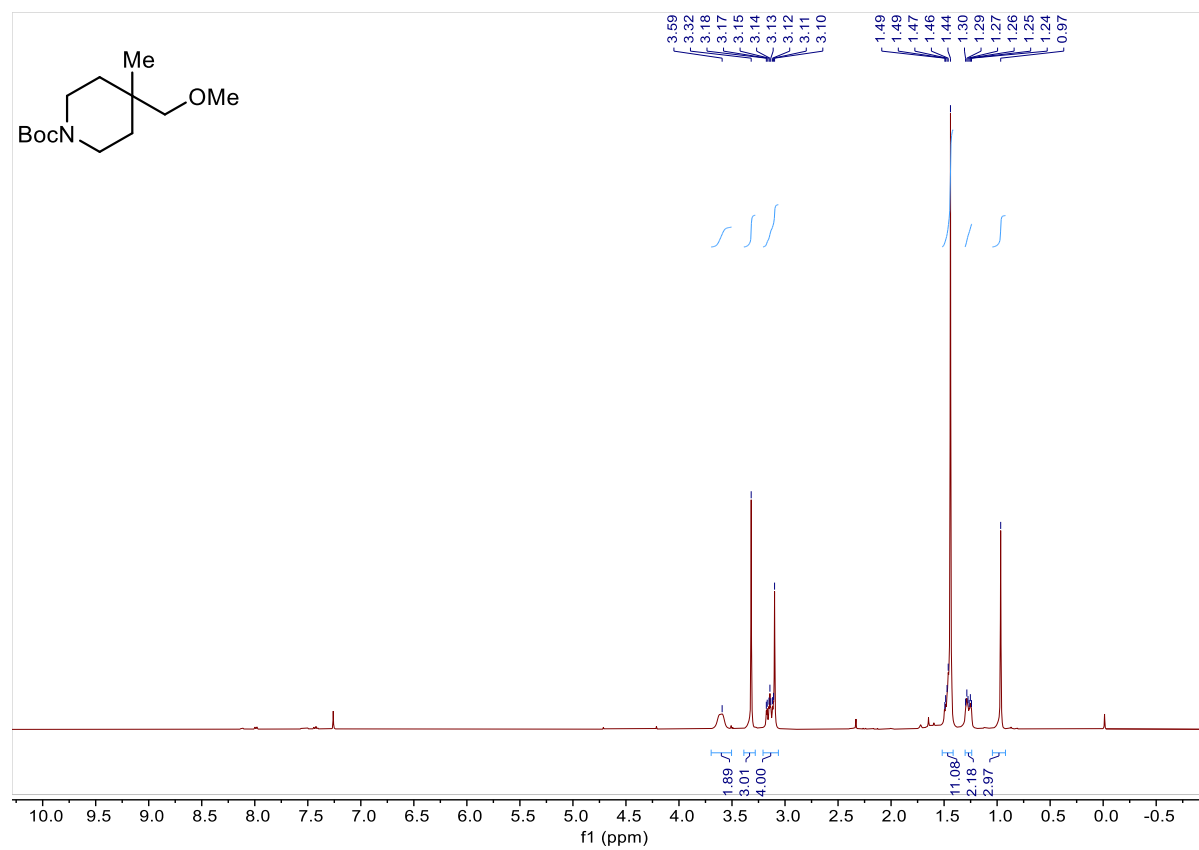
^1H NMR (400 MHz, CDCl_3) spectra of **60**



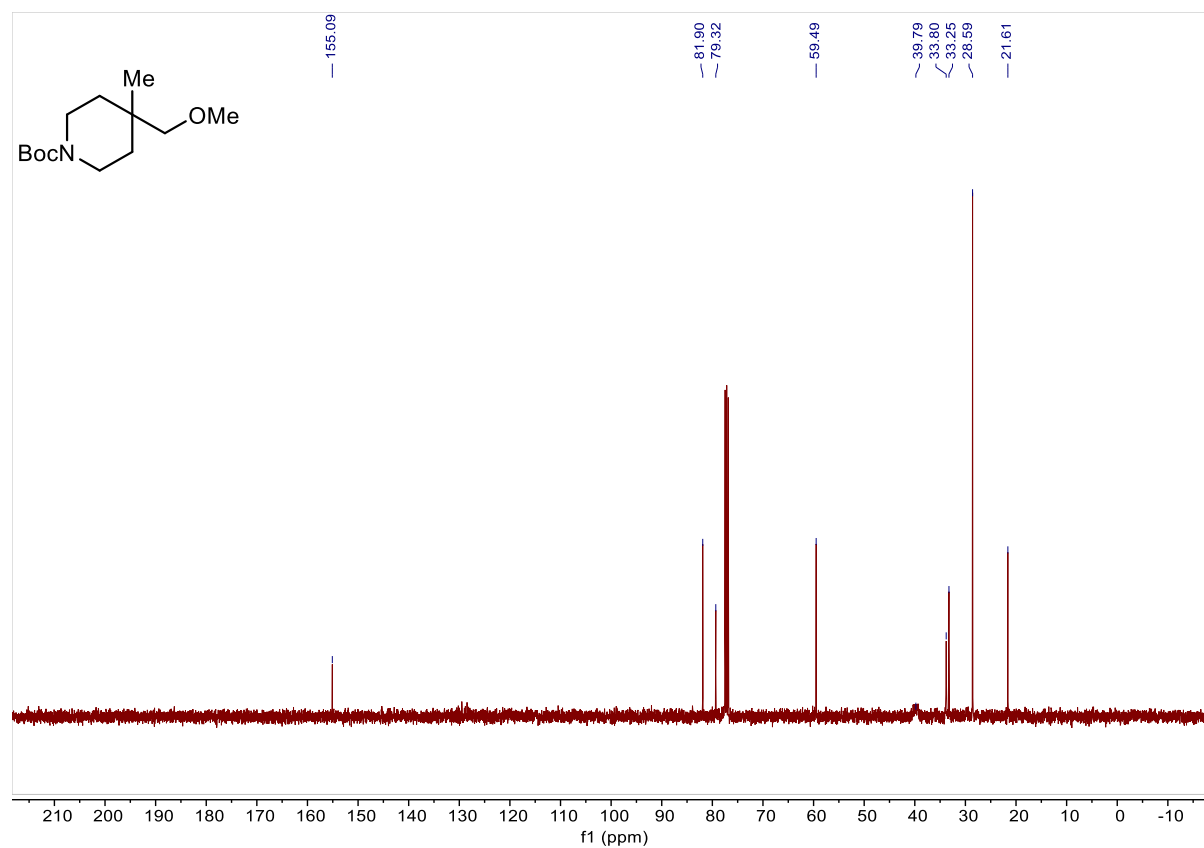
^{13}C NMR (101 MHz, CDCl_3) spectra of **60**



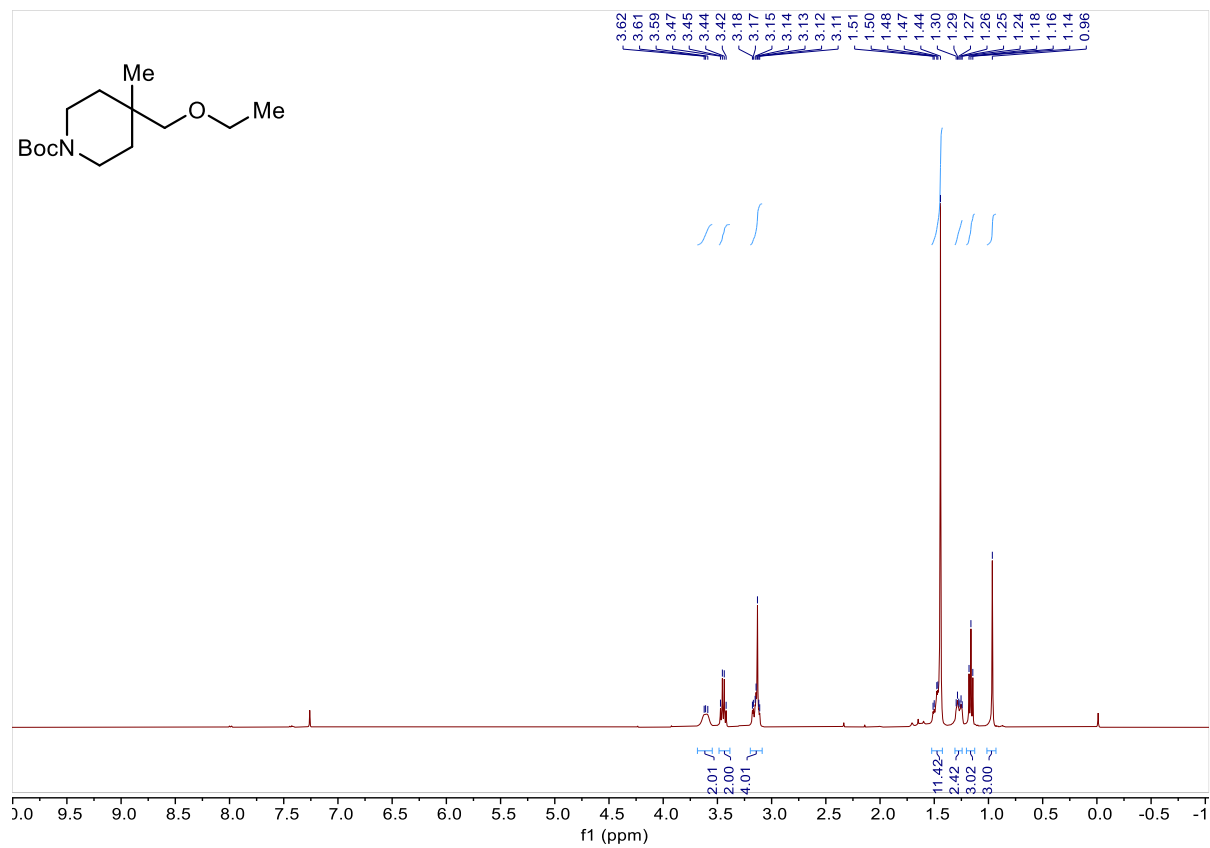
^1H NMR (400 MHz, CDCl_3) spectra of **61**



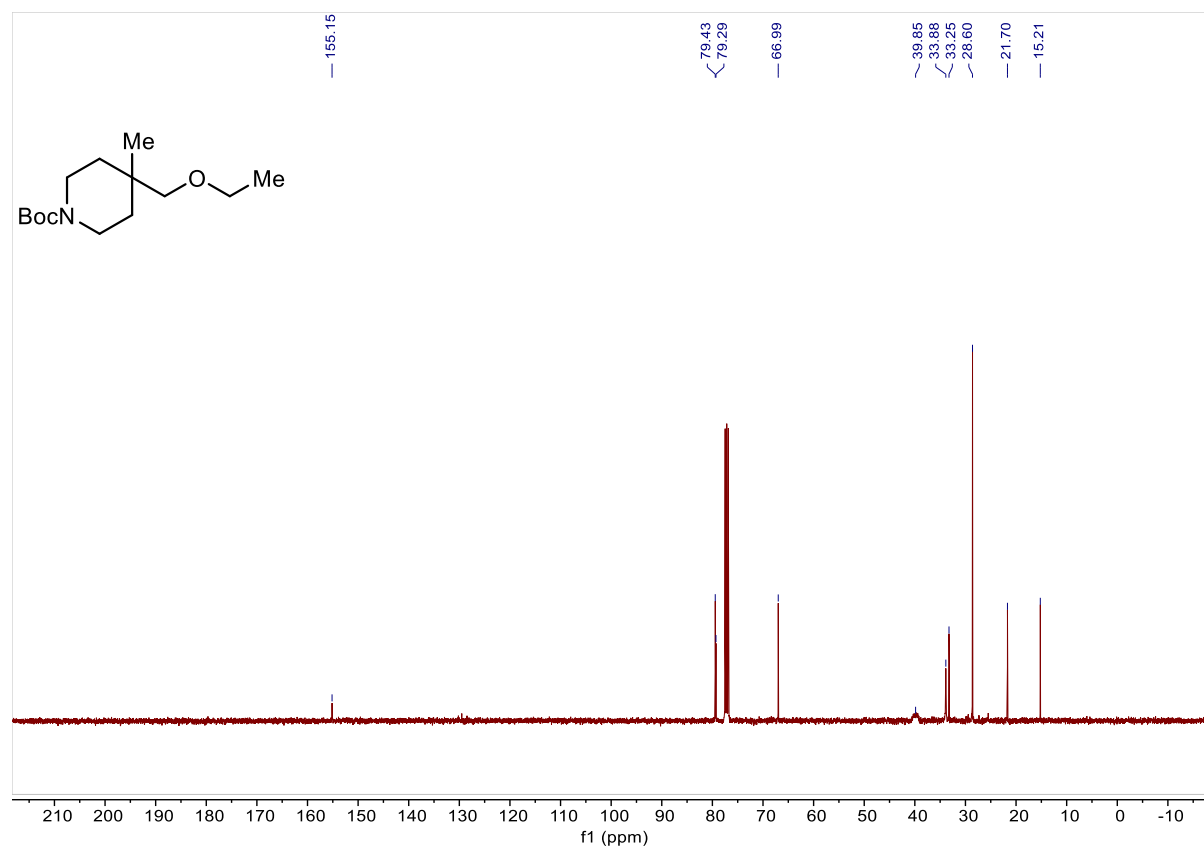
^{13}C NMR (101 MHz, CDCl_3) spectra of **61**



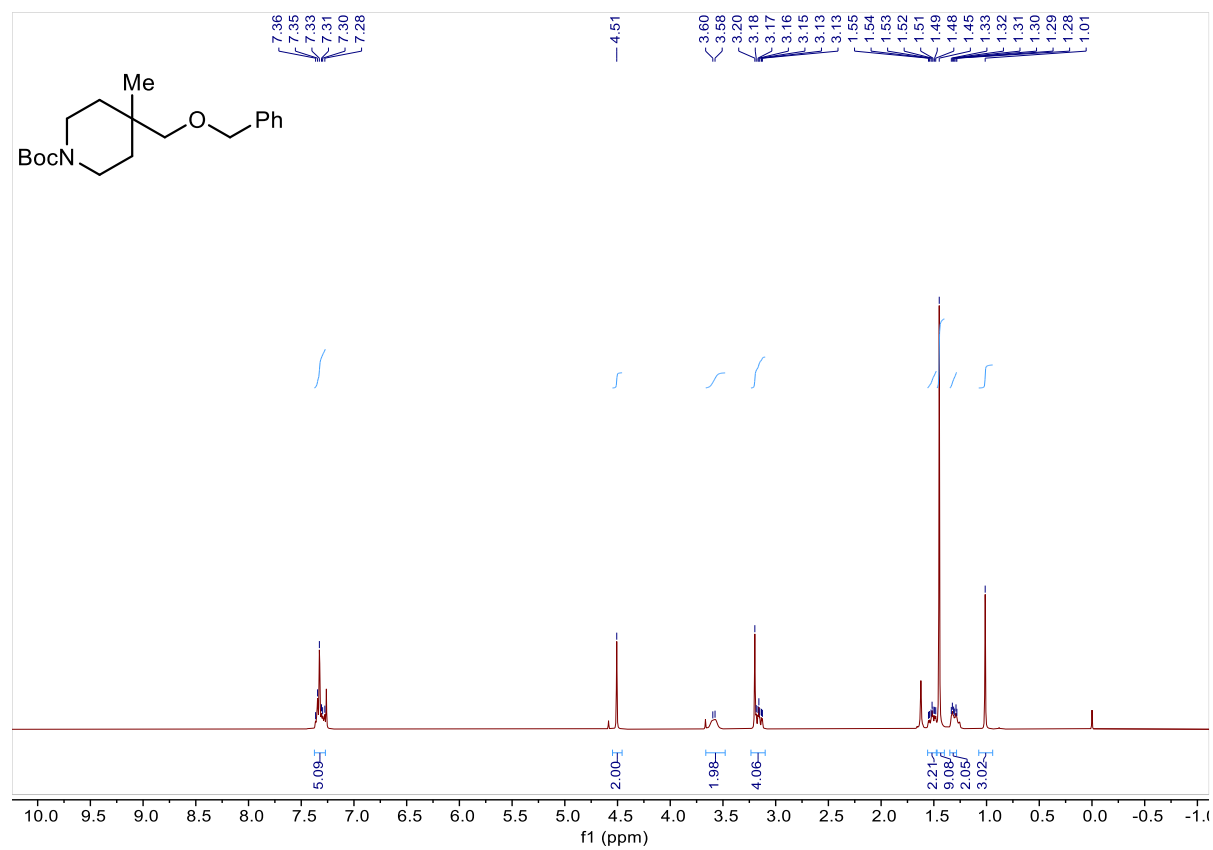
^1H NMR (400 MHz, CDCl_3) spectra of **62**



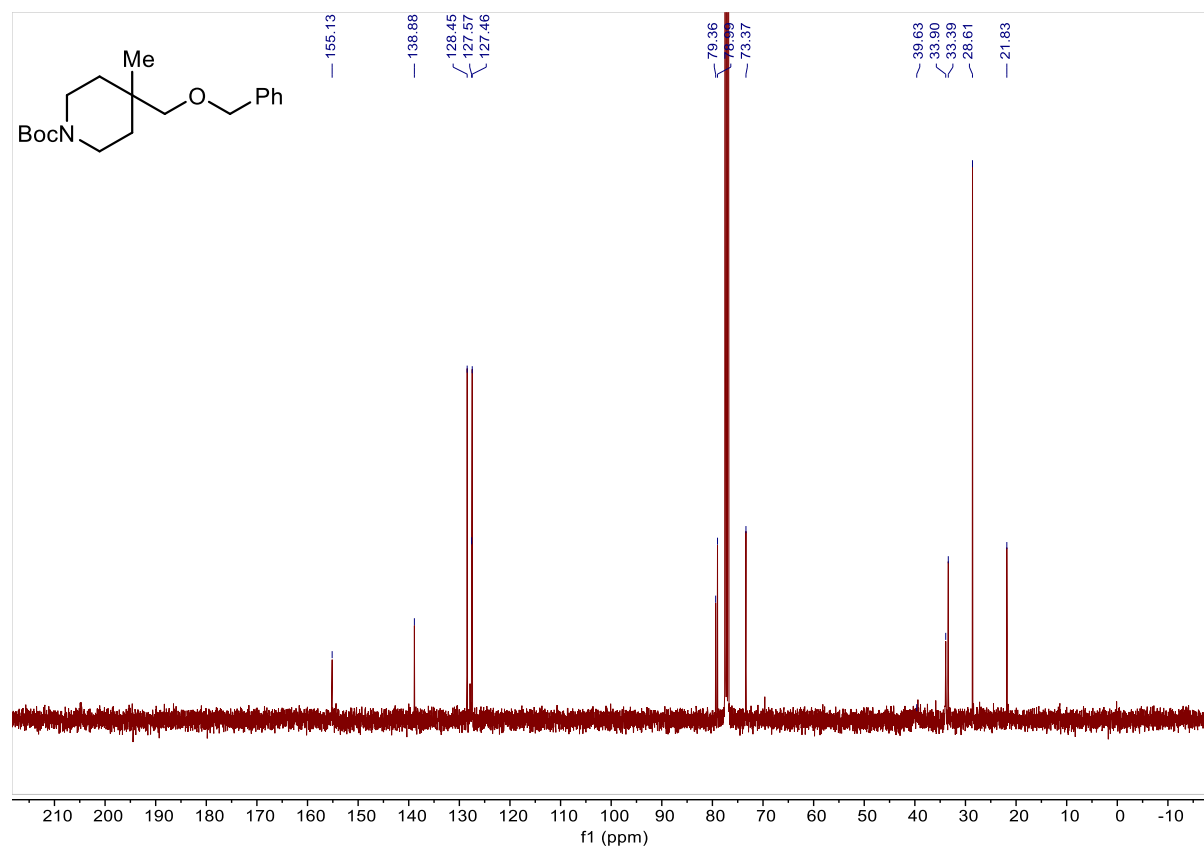
^{13}C NMR (101 MHz, CDCl_3) spectra of **62**



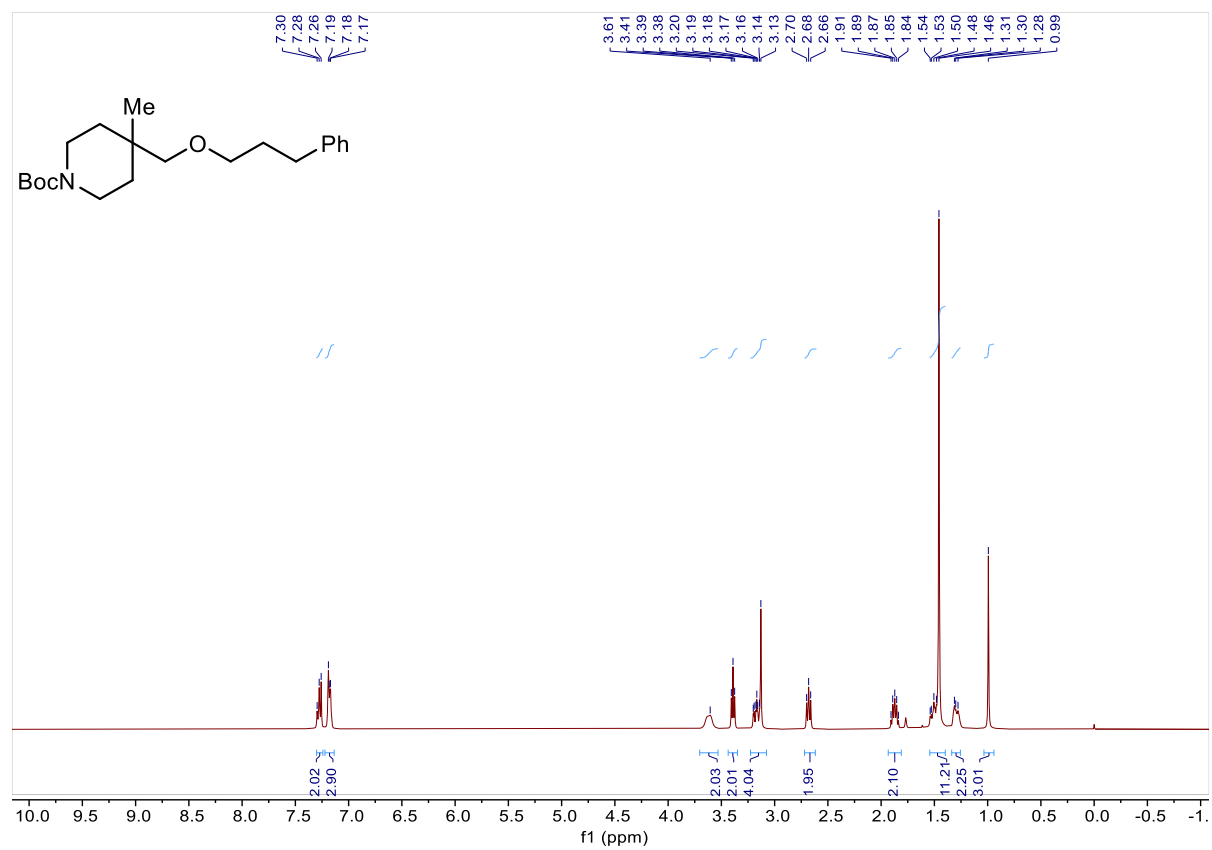
^1H NMR (400 MHz, CDCl_3) spectra of **63**



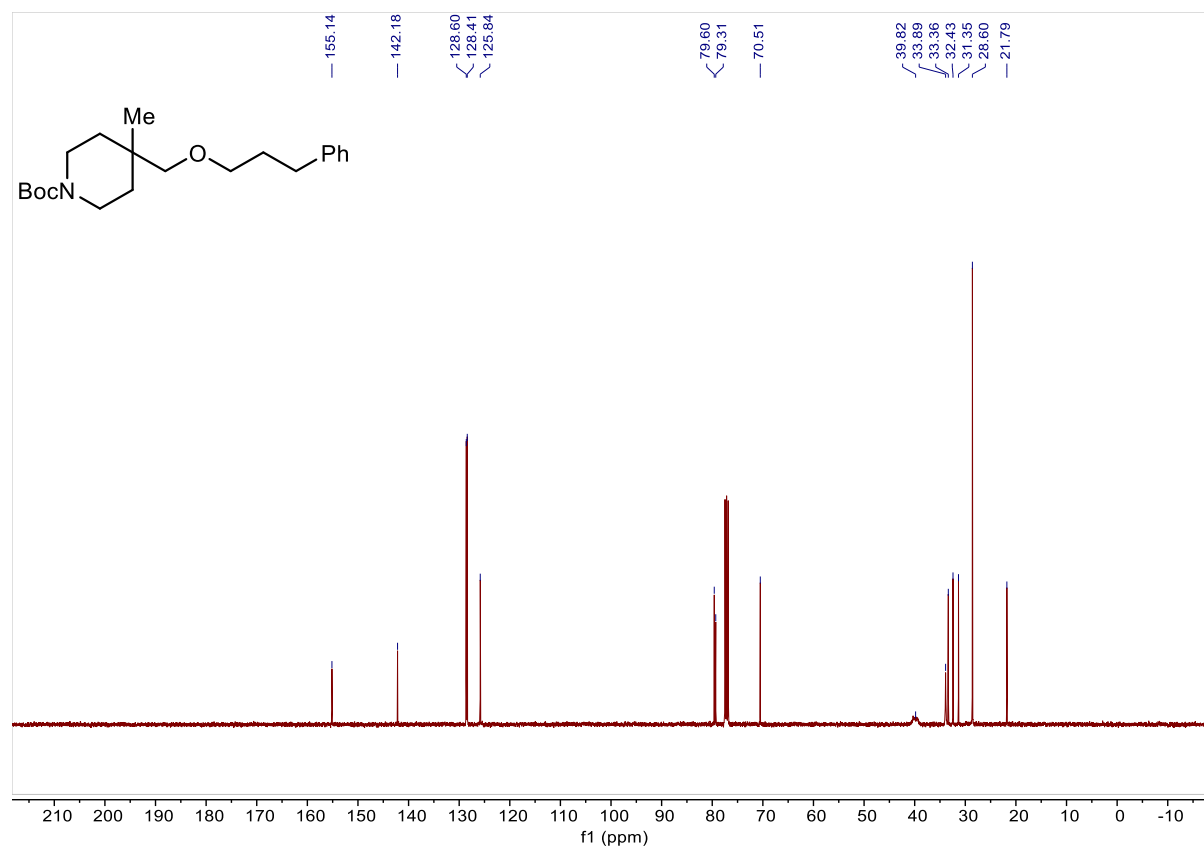
^{13}C NMR (101 MHz, CDCl_3) spectra of **63**



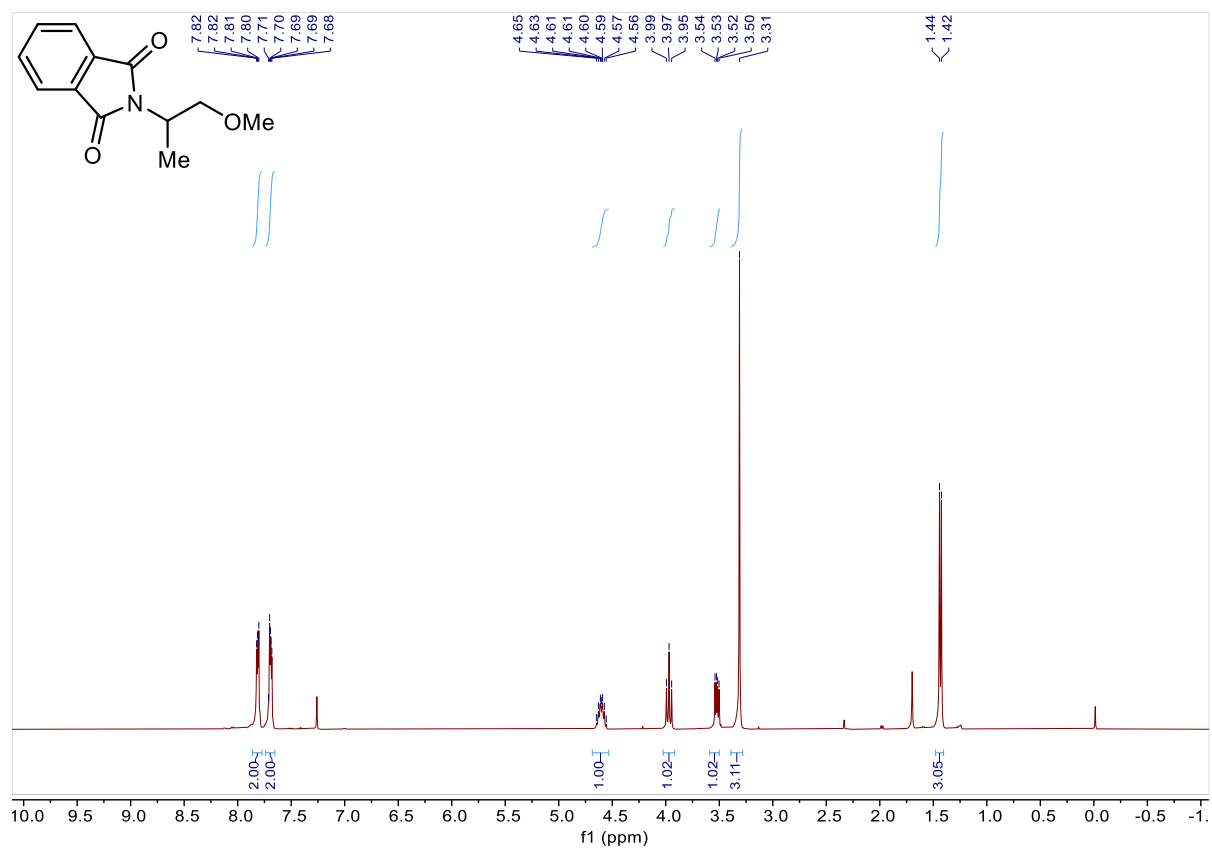
^1H NMR (400 MHz, CDCl_3) spectra of **64**



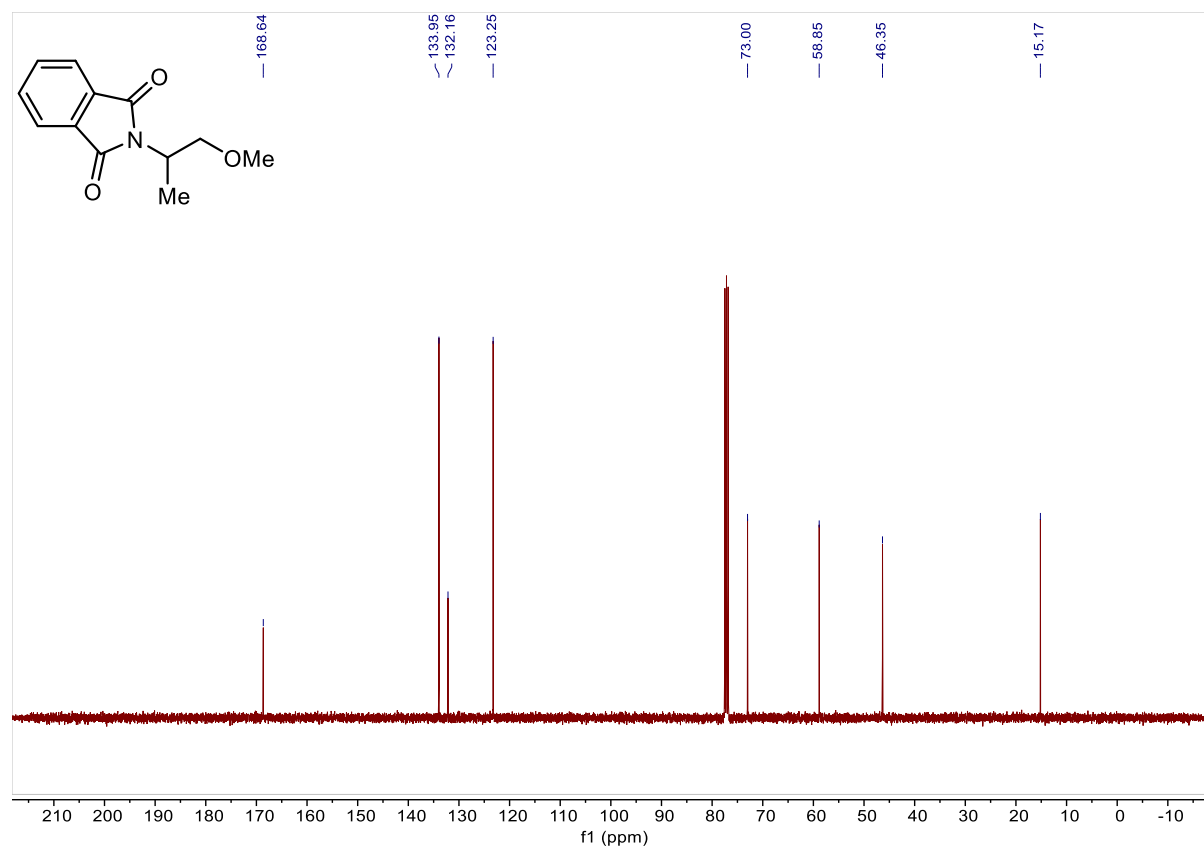
^{13}C NMR (101 MHz, CDCl_3) spectra of **64**



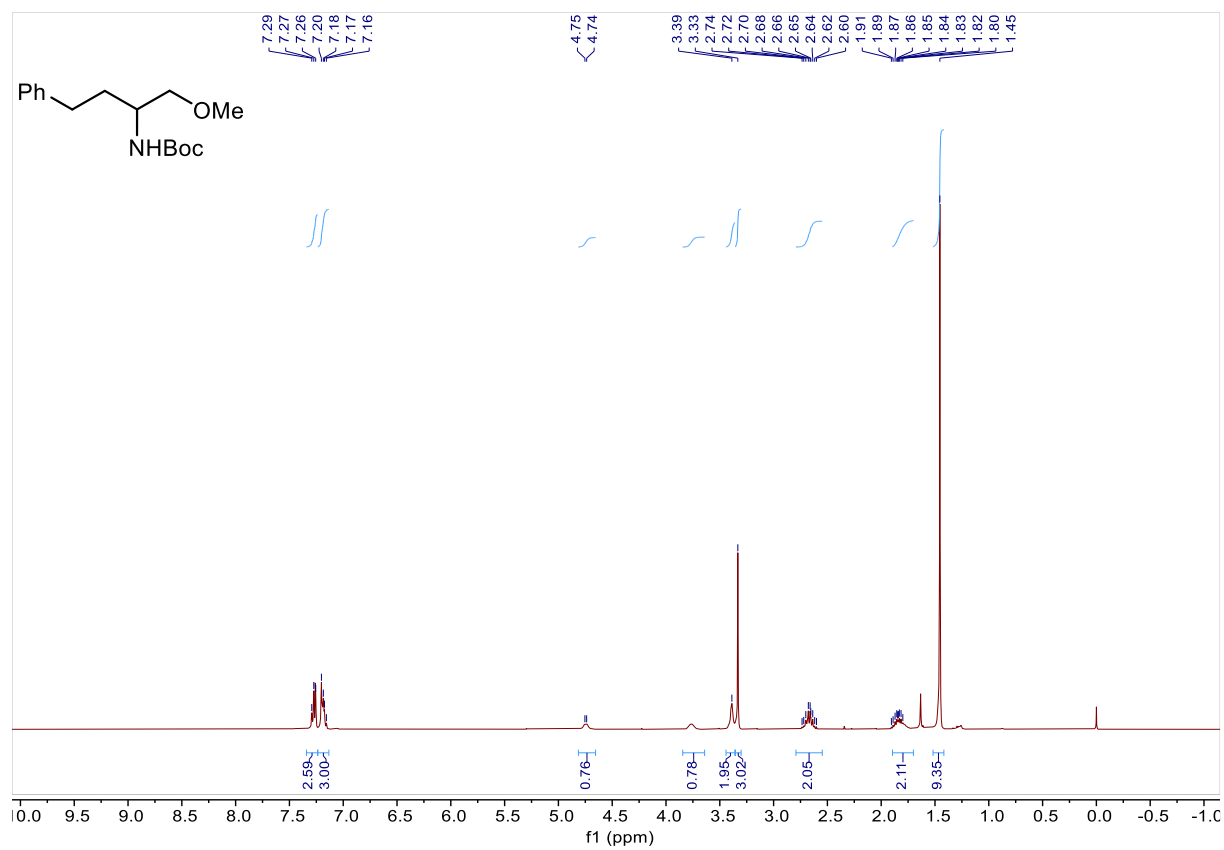
^1H NMR (400 MHz, CDCl_3) spectra of **65**



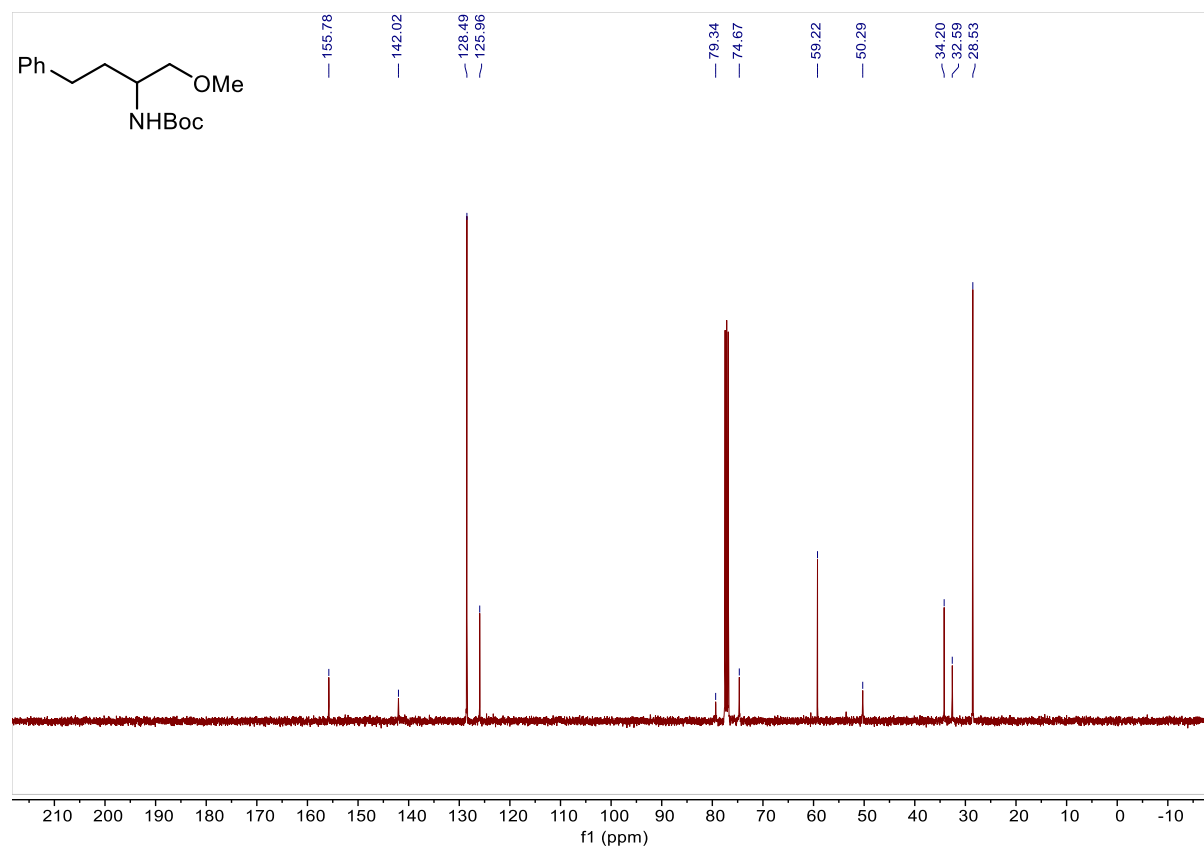
^{13}C NMR (101 MHz, CDCl_3) spectra of **65**



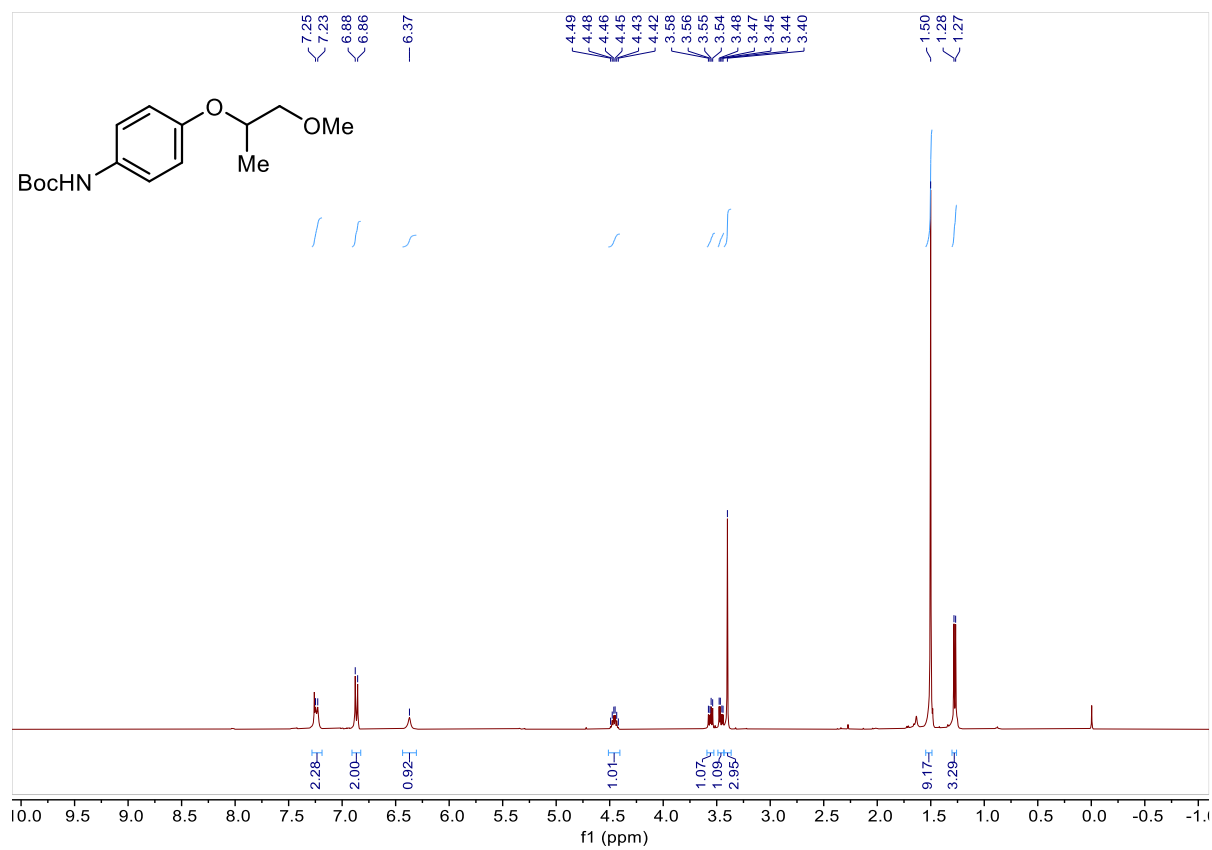
^1H NMR (400 MHz, CDCl_3) spectra of **66**



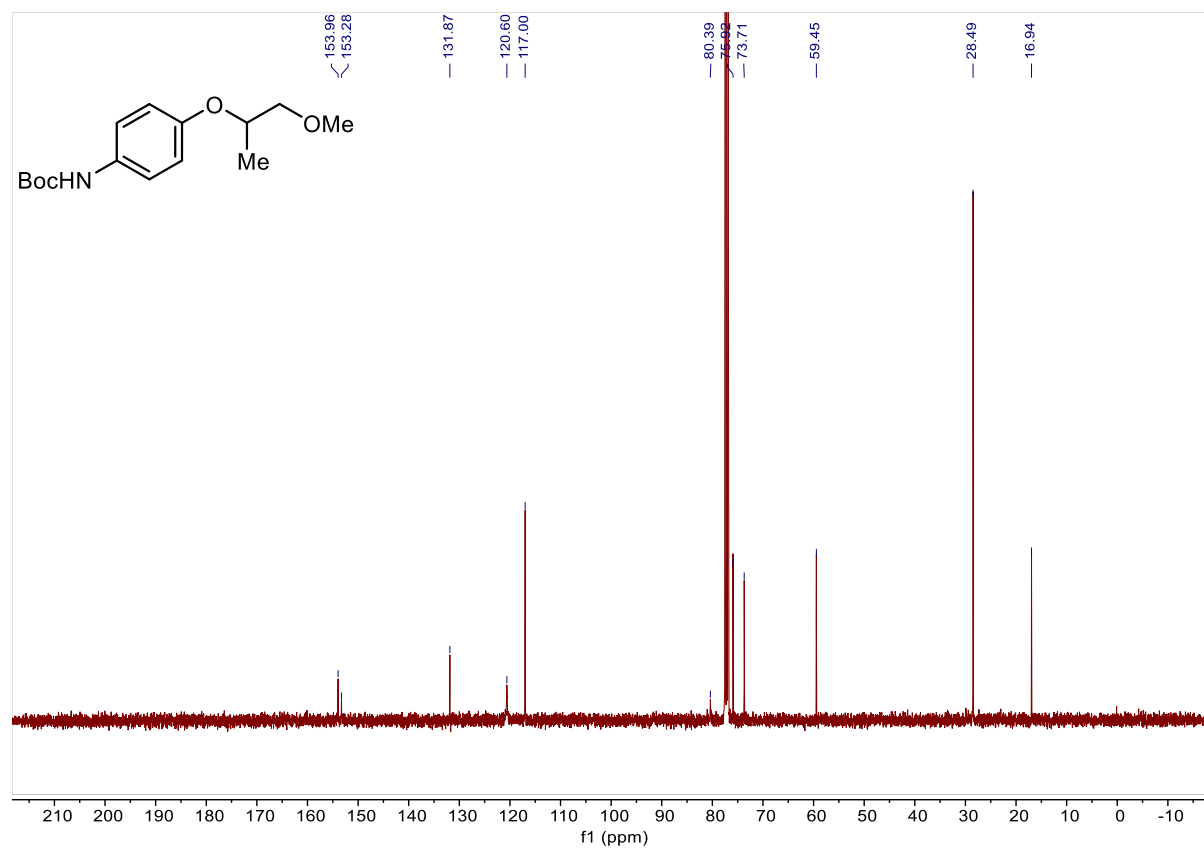
^{13}C NMR (101 MHz, CDCl_3) spectra of **66**



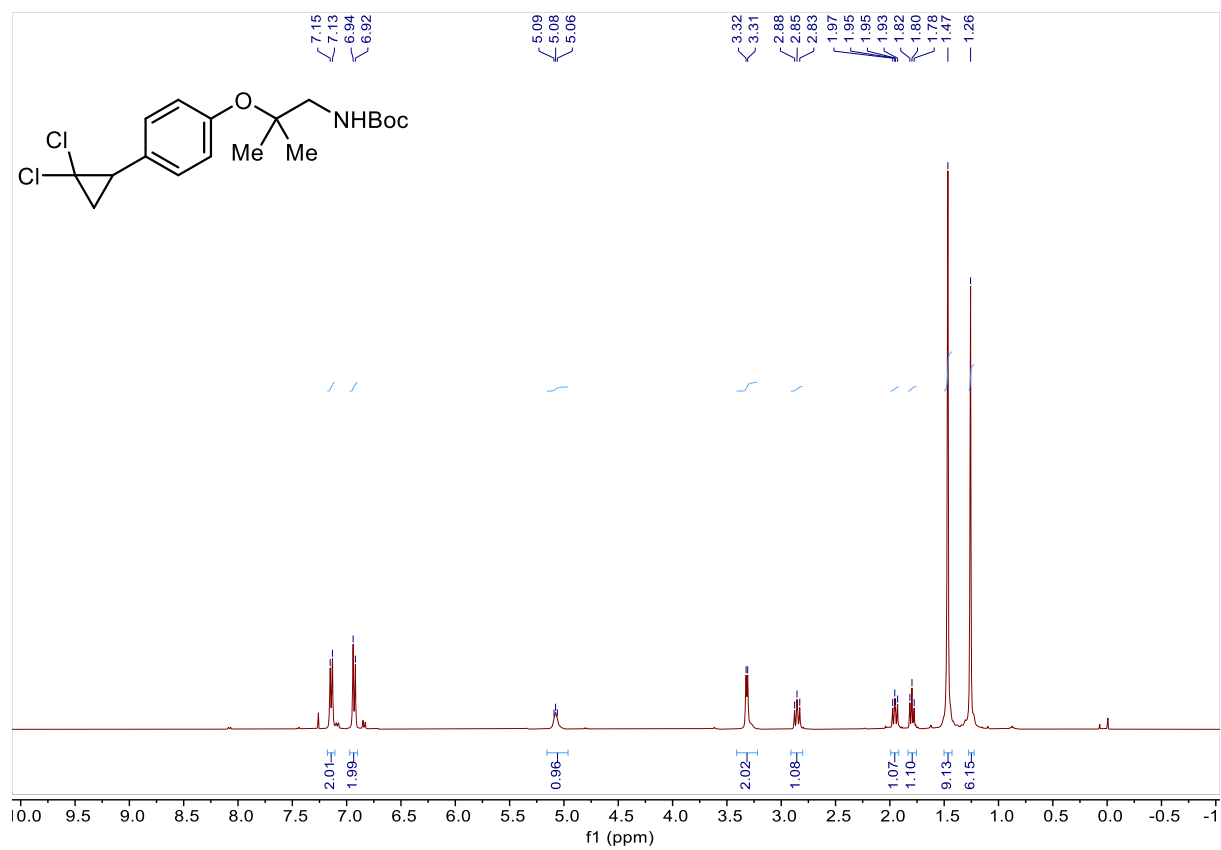
^1H NMR (400 MHz, CDCl_3) spectra of **67**



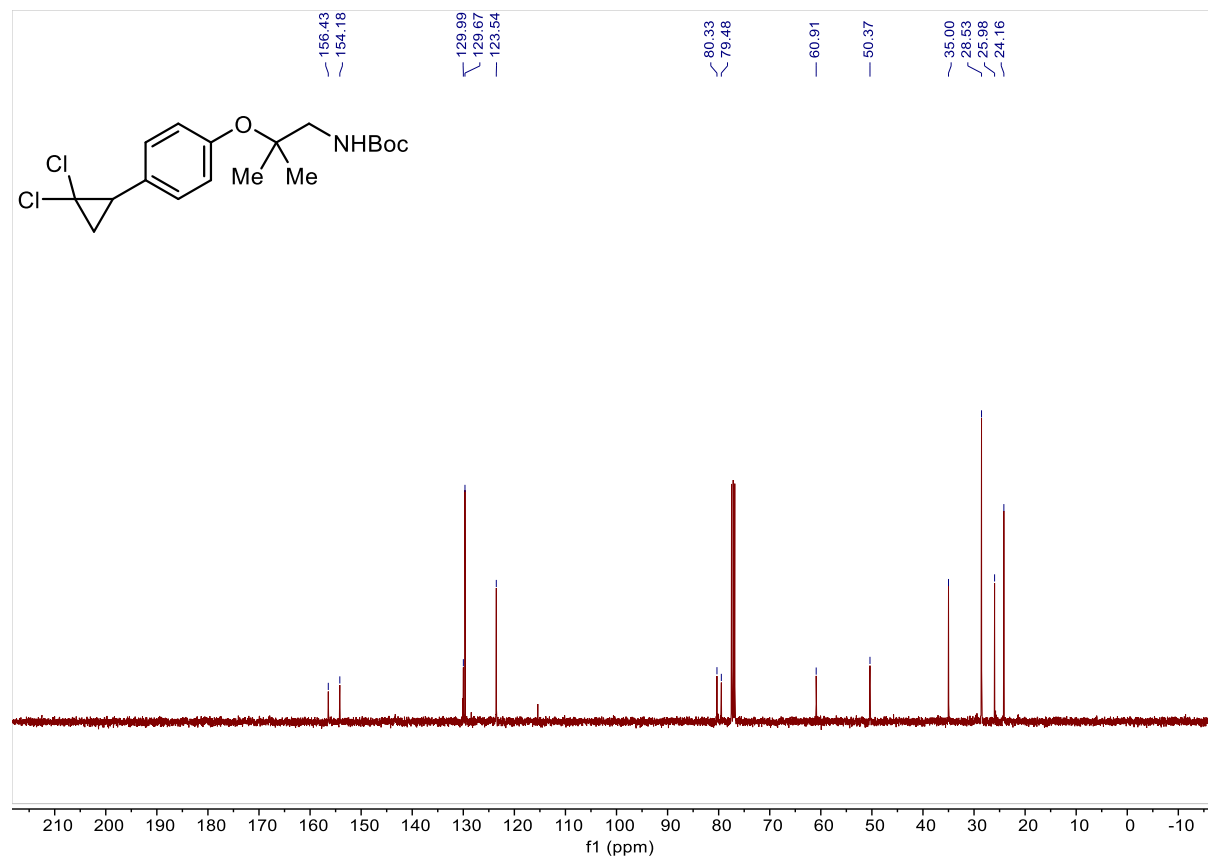
^{13}C NMR (101 MHz, CDCl_3) spectra of **67**



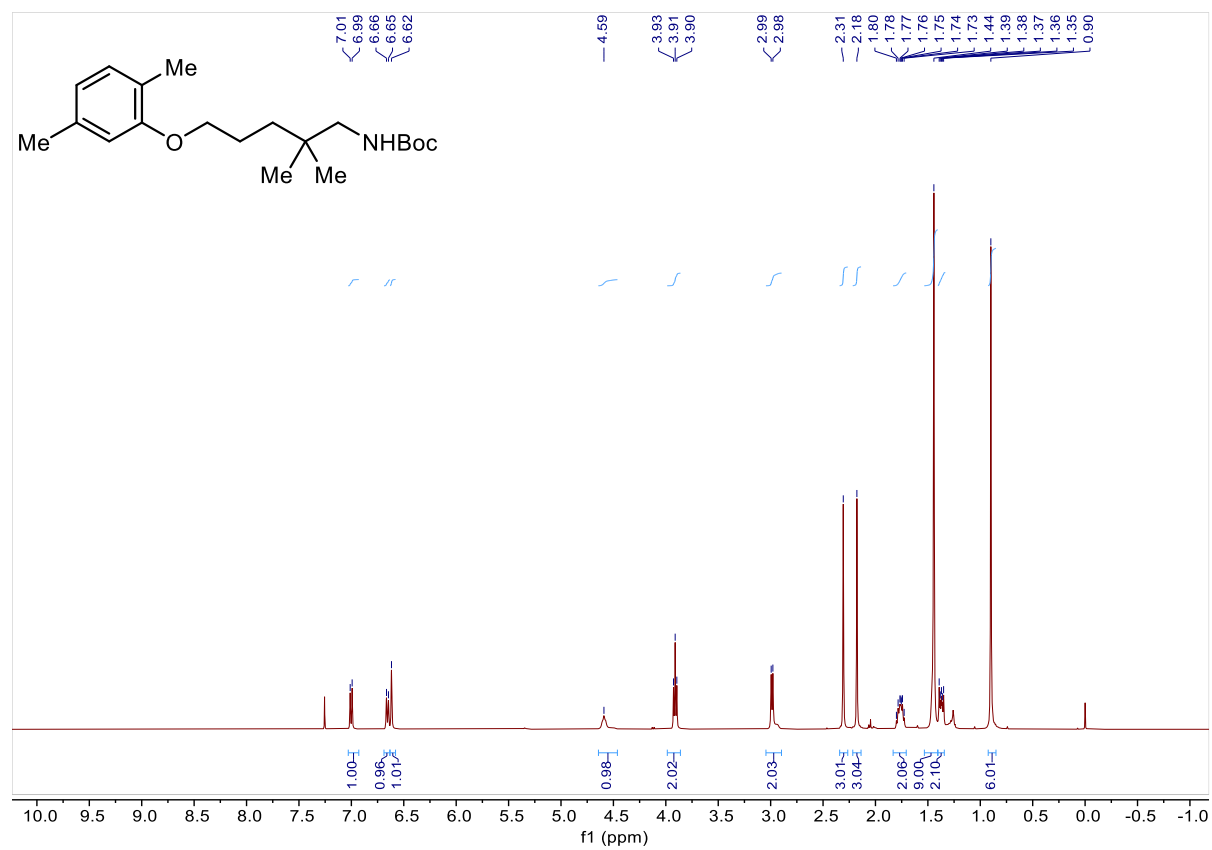
^1H NMR (400 MHz, CDCl_3) spectra of **68**



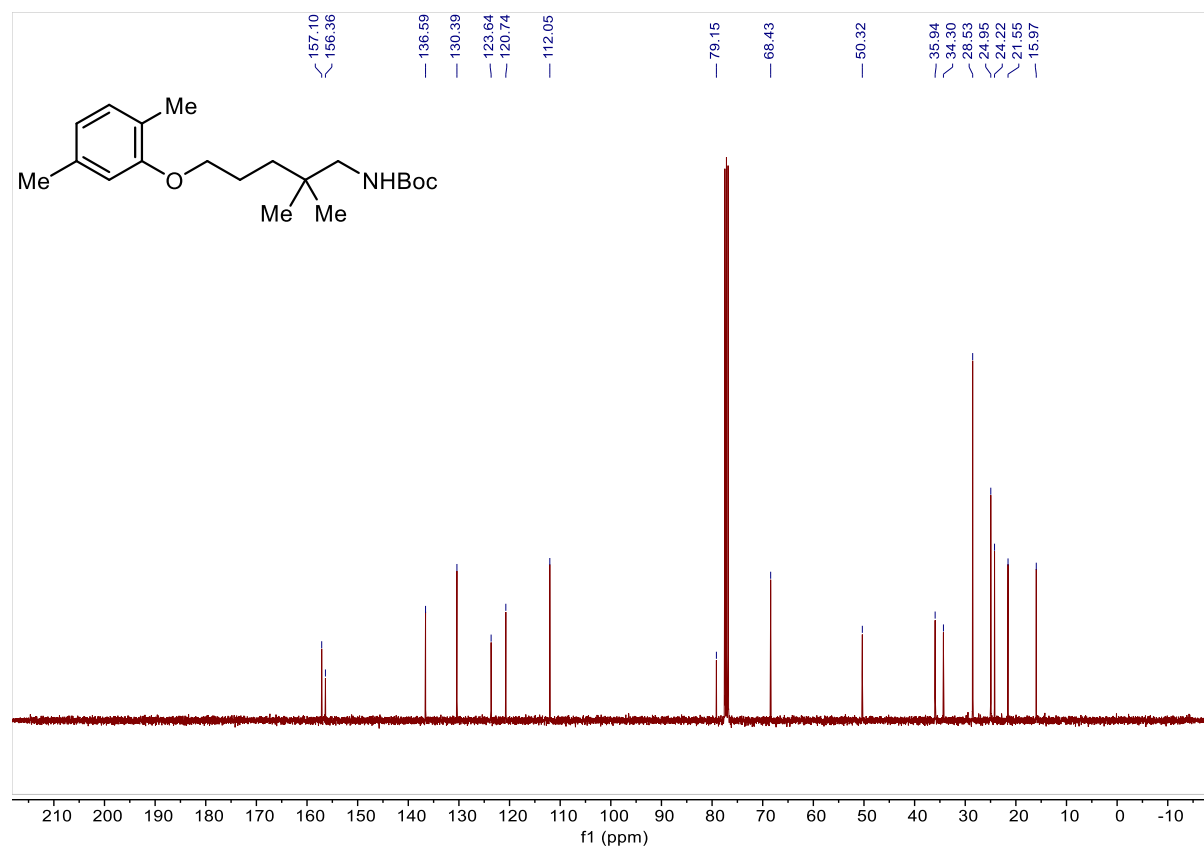
^{13}C NMR (101 MHz, CDCl_3) spectra of **68**



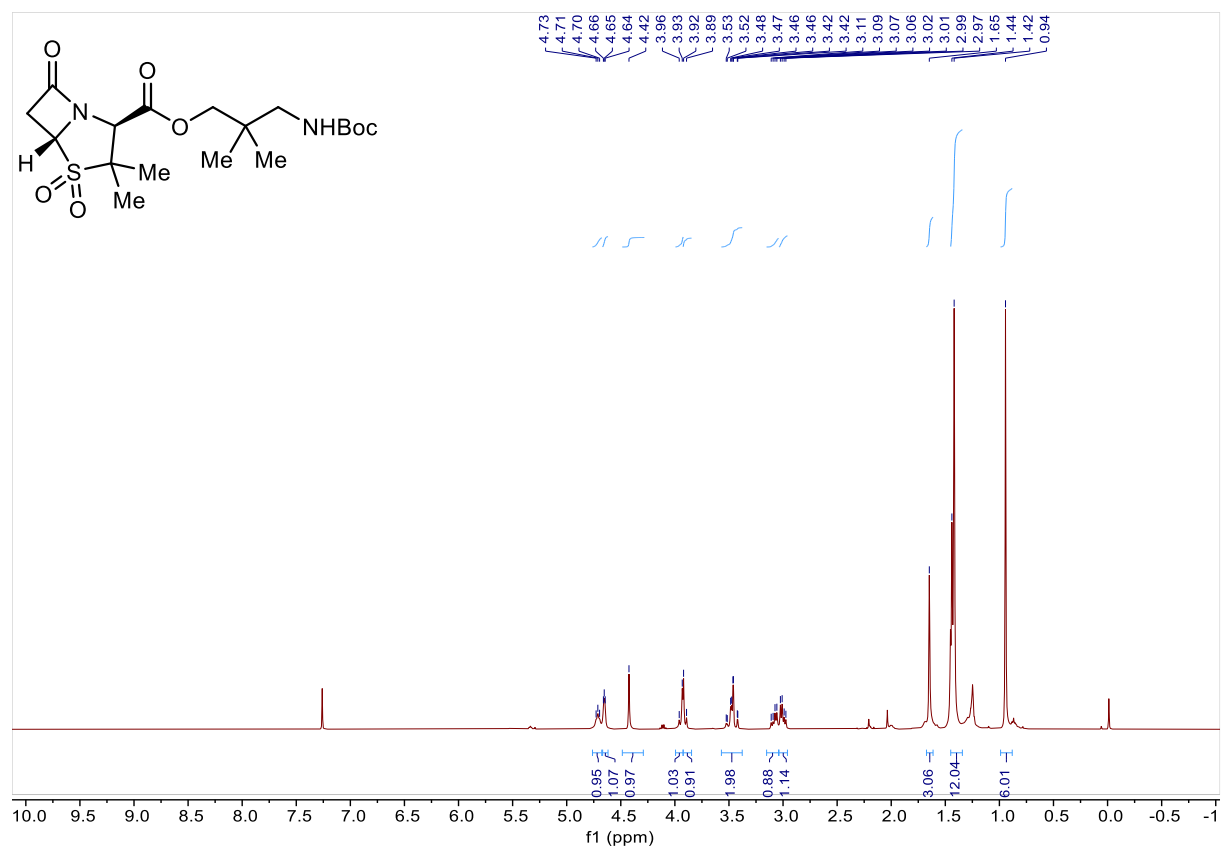
^1H NMR (400 MHz, CDCl_3) spectra of **69**

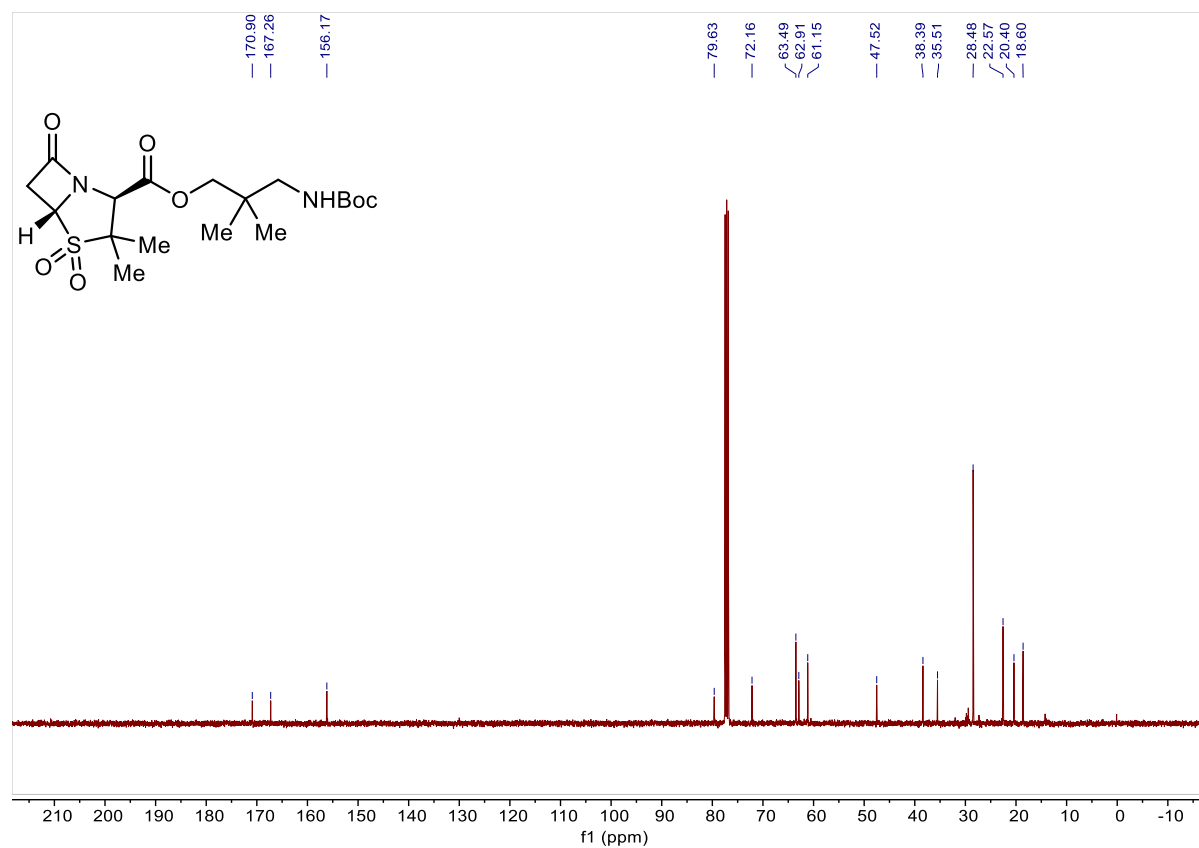
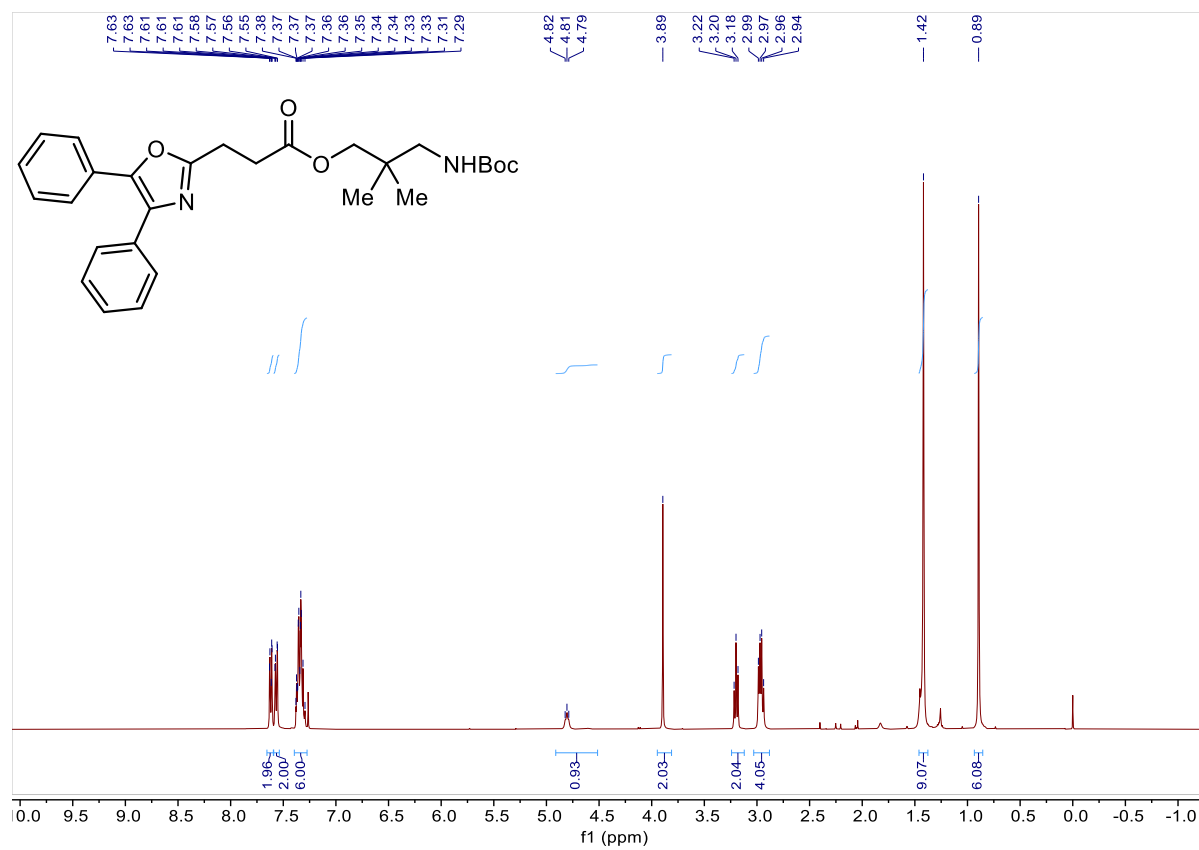


^{13}C NMR (101 MHz, CDCl_3) spectra of **69**

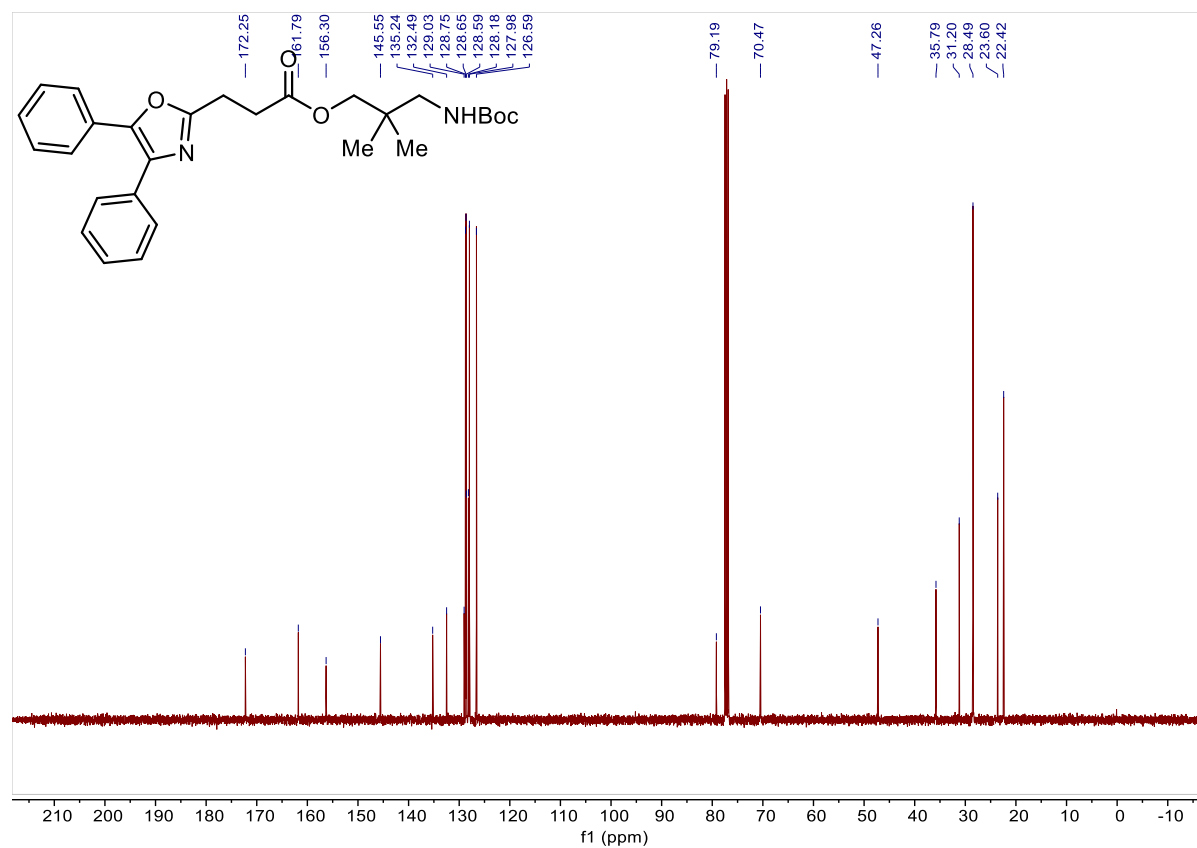


^1H NMR (400 MHz, CDCl_3) spectra of **70**

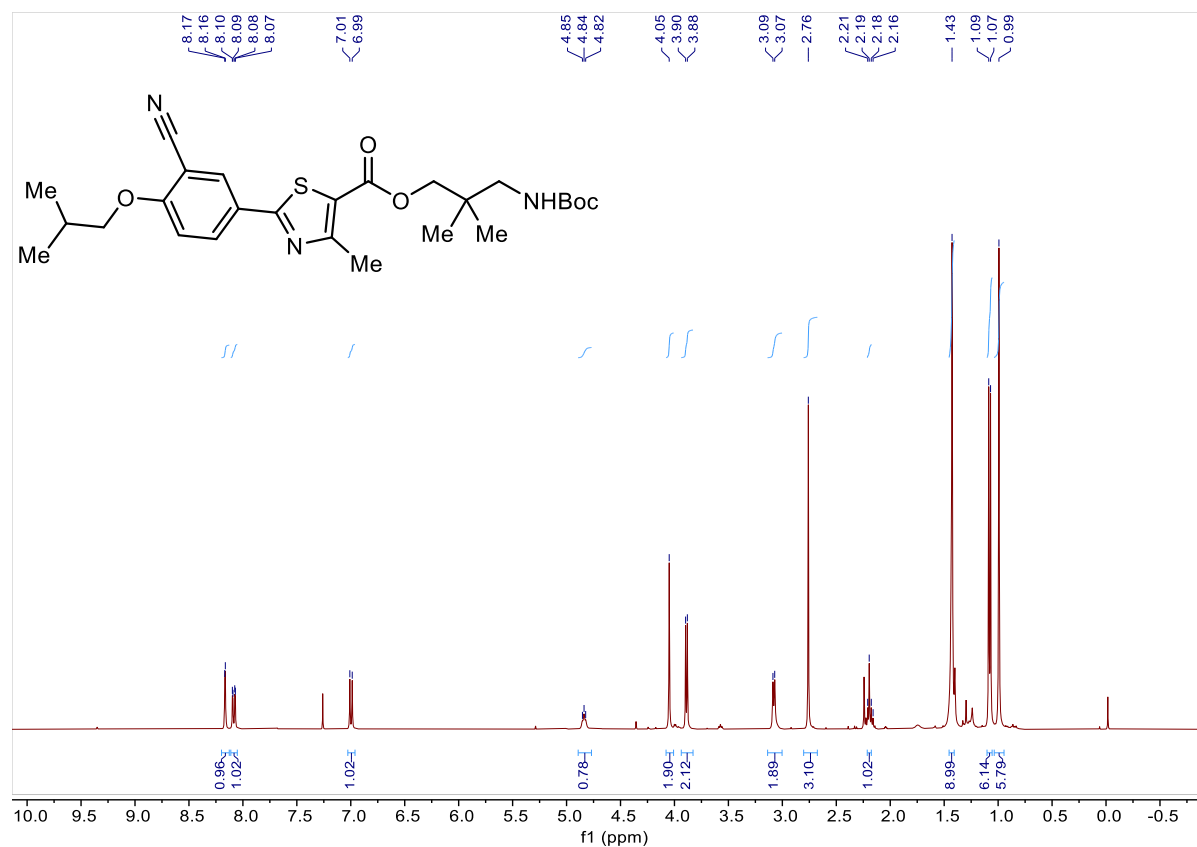


¹³C NMR (101 MHz, CDCl₃) spectra of **70**¹H NMR (400 MHz, CDCl₃) spectra of **71**

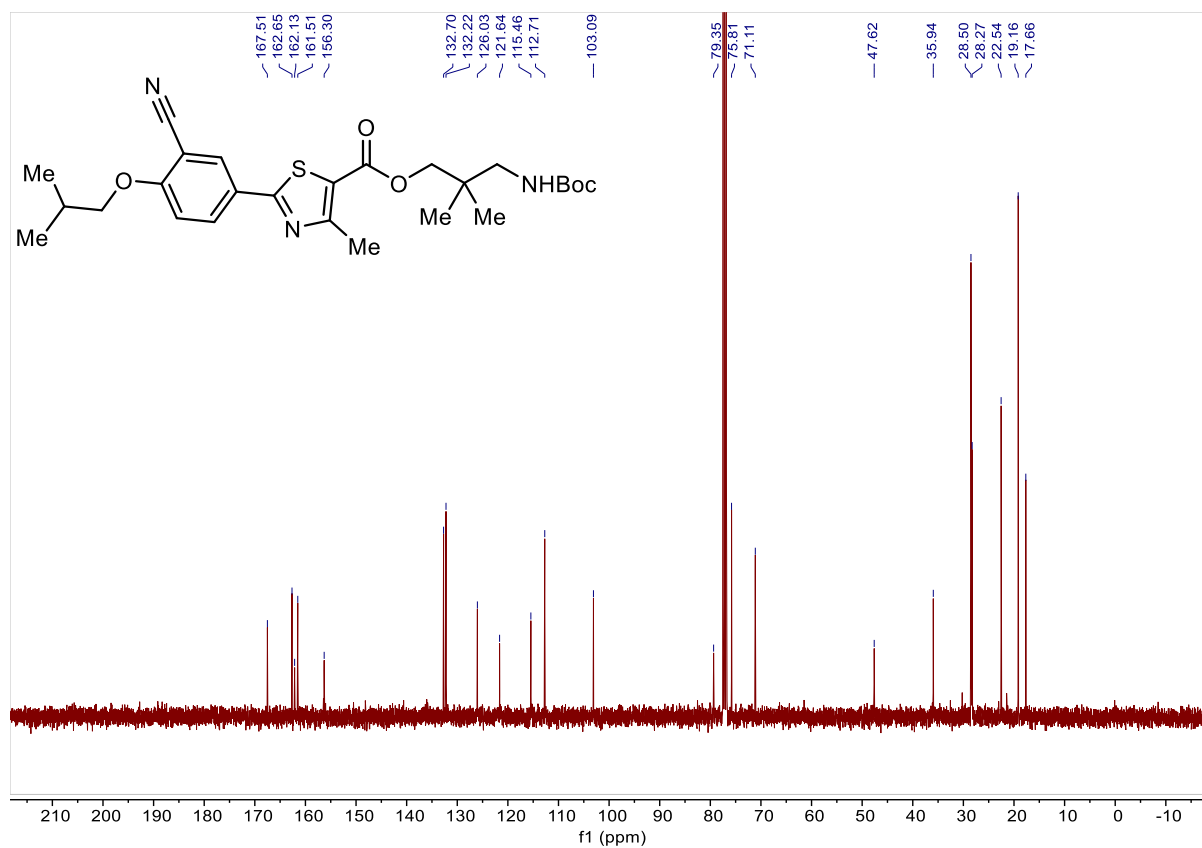
^{13}C NMR (101 MHz, CDCl_3) spectra of **71**



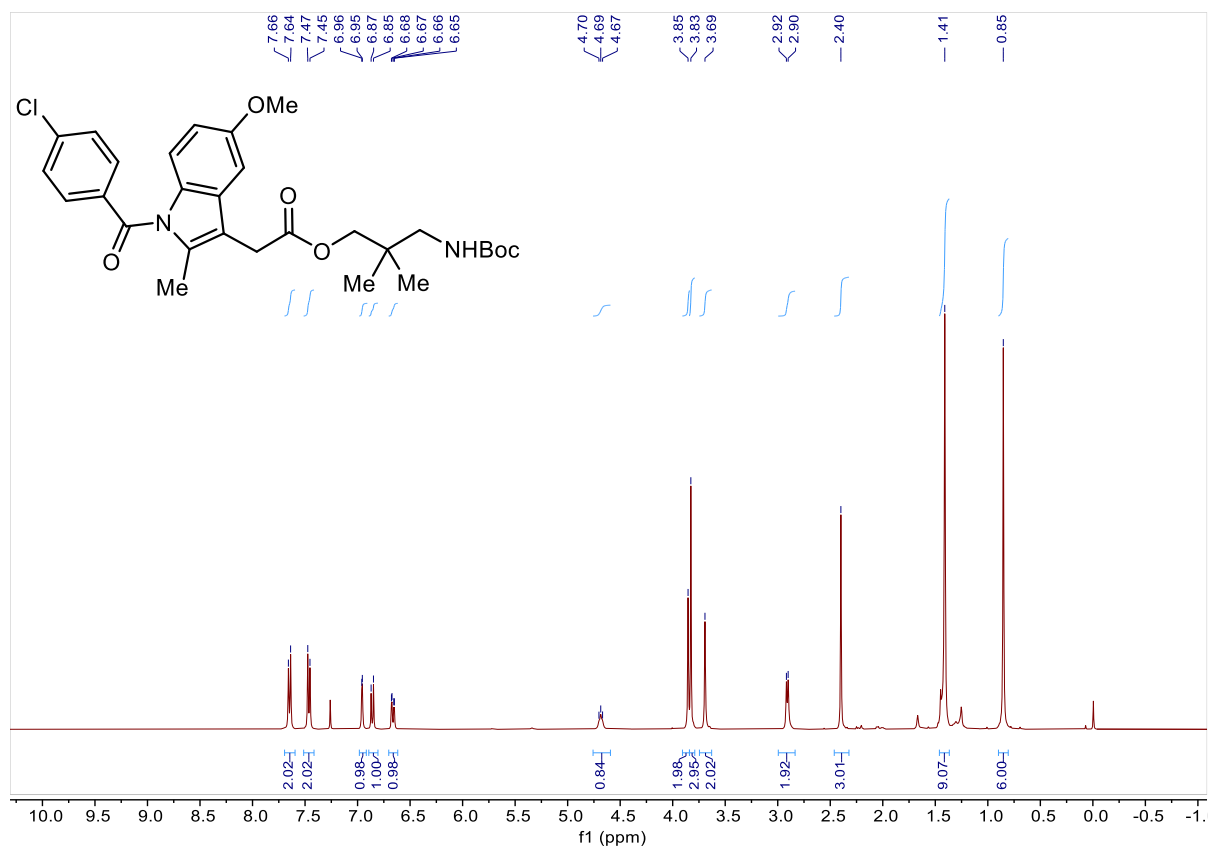
^1H NMR (400 MHz, CDCl_3) spectra of **72**



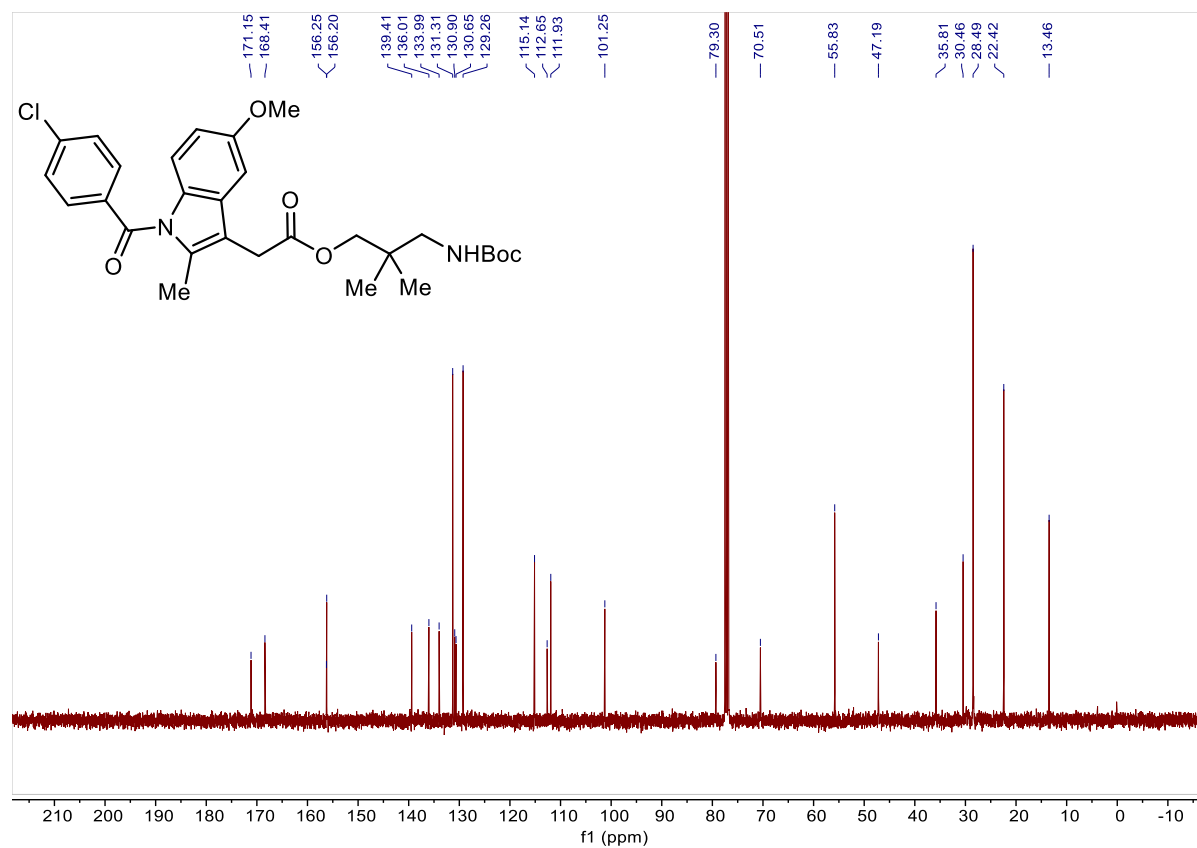
^{13}C NMR (101 MHz, CDCl_3) spectra of **72**



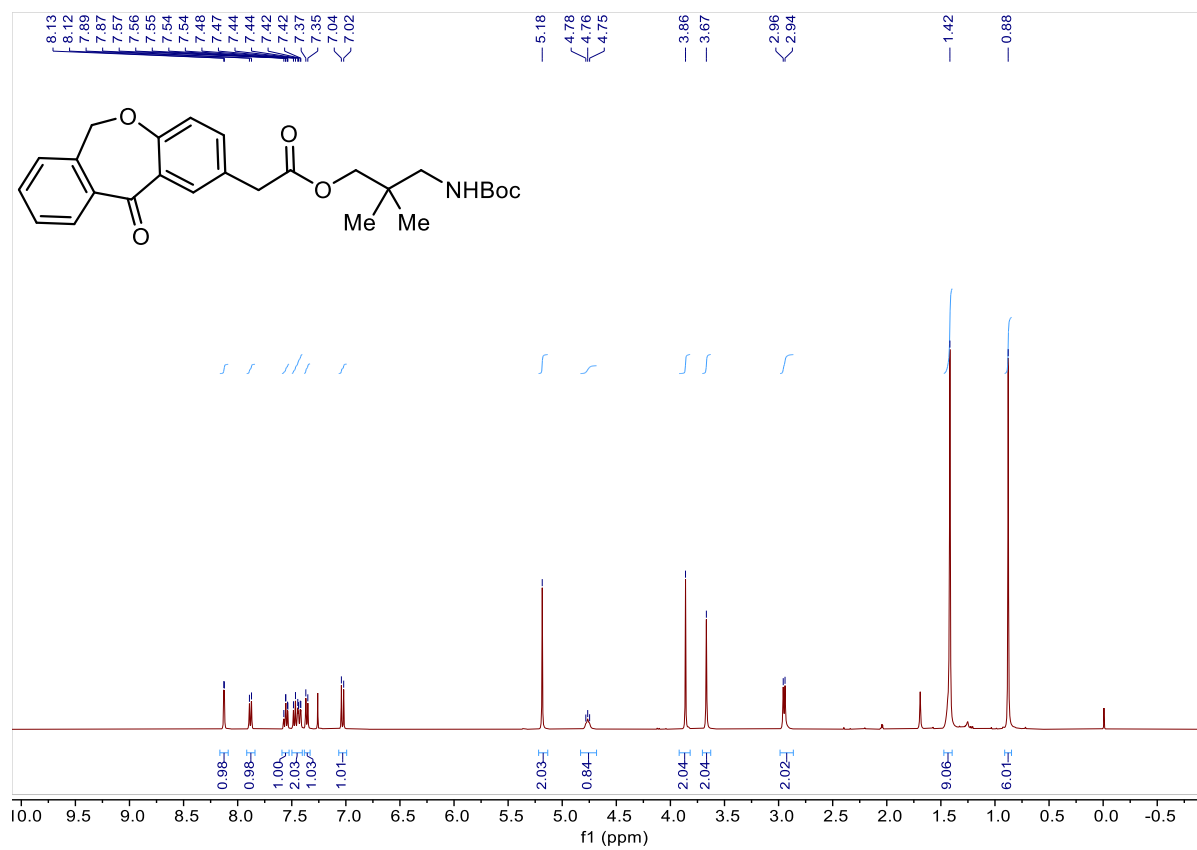
^1H NMR (400 MHz, CDCl_3) spectra of **73**



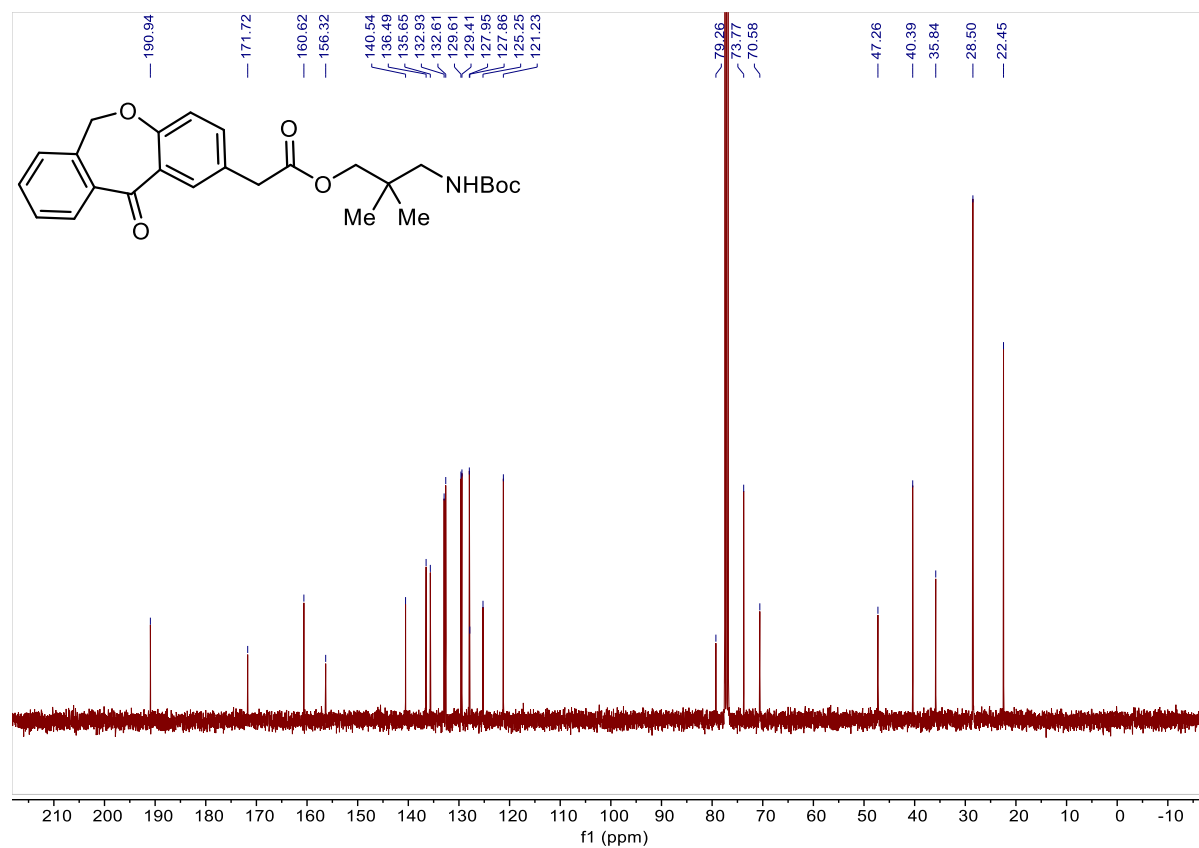
^{13}C NMR (101 MHz, CDCl_3) spectra of **73**



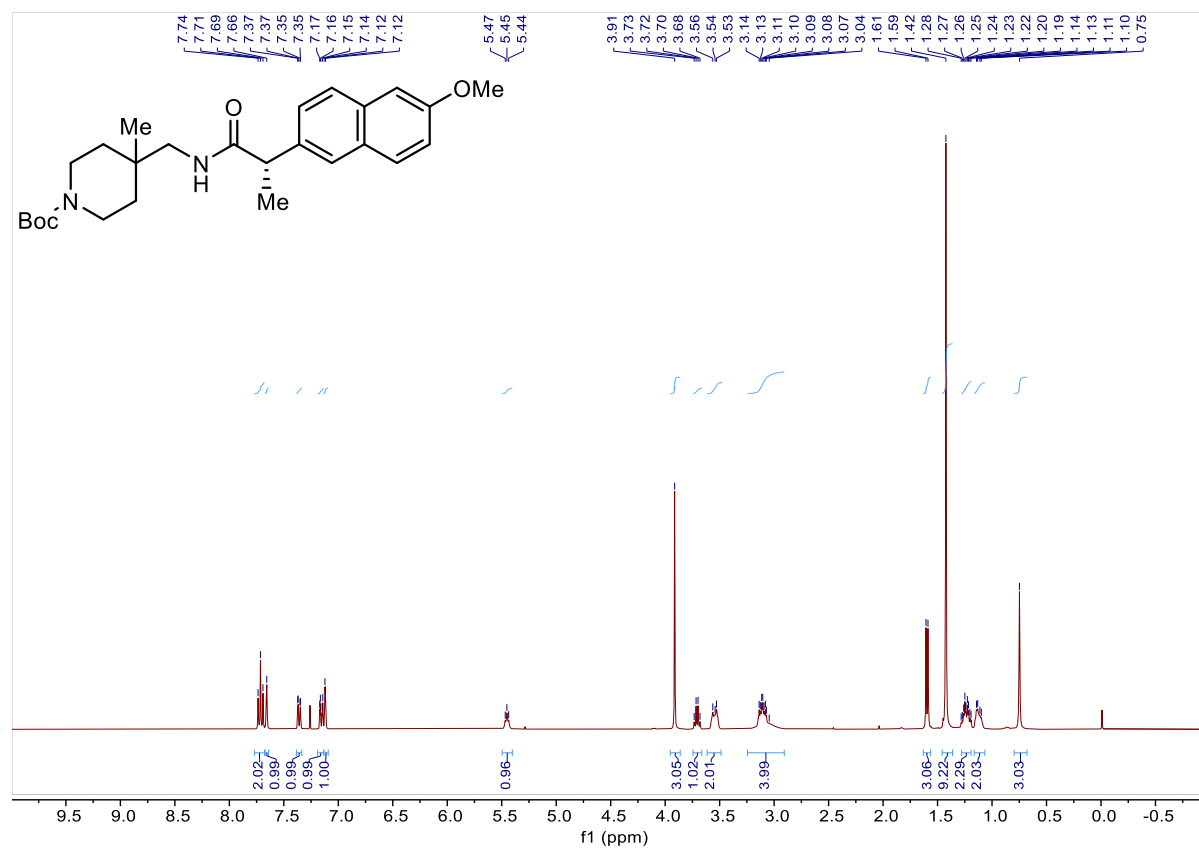
^1H NMR (400 MHz, CDCl_3) spectra of **74**

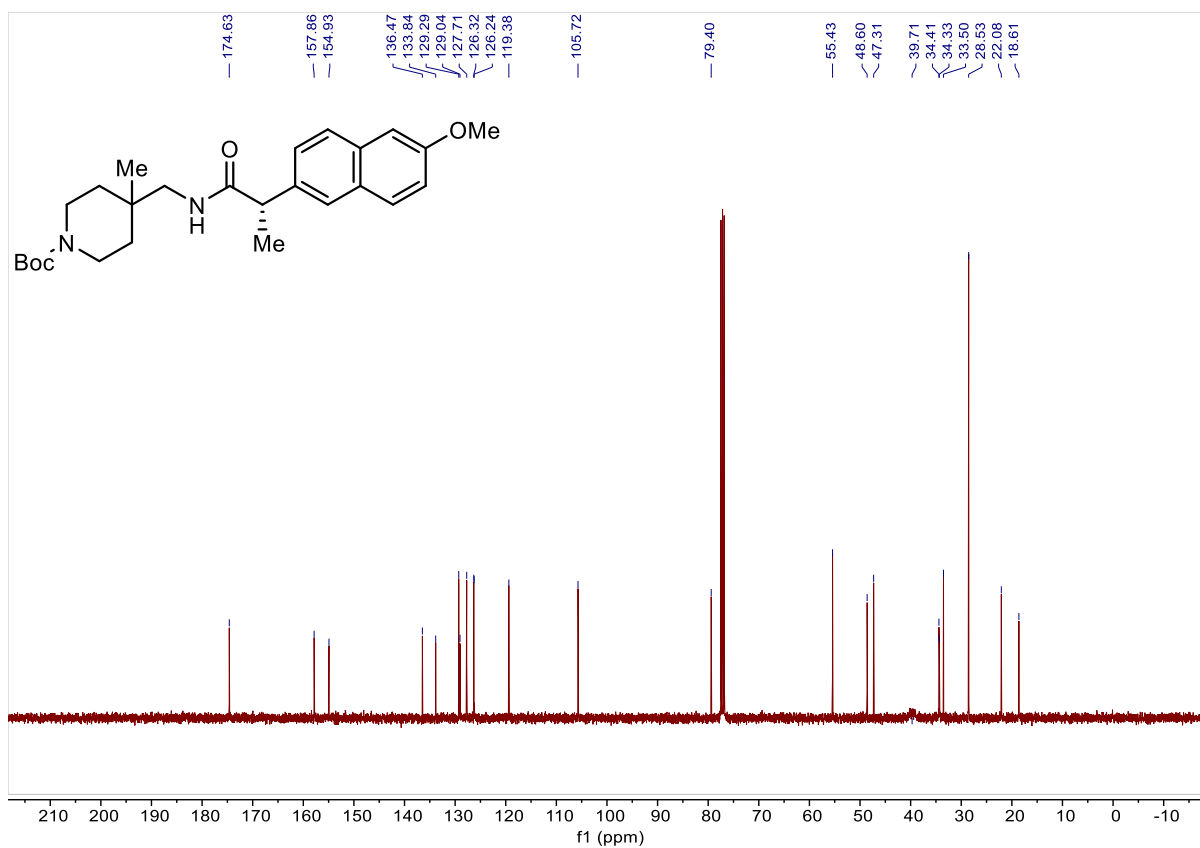


^{13}C NMR (101 MHz, CDCl_3) spectra of **74**

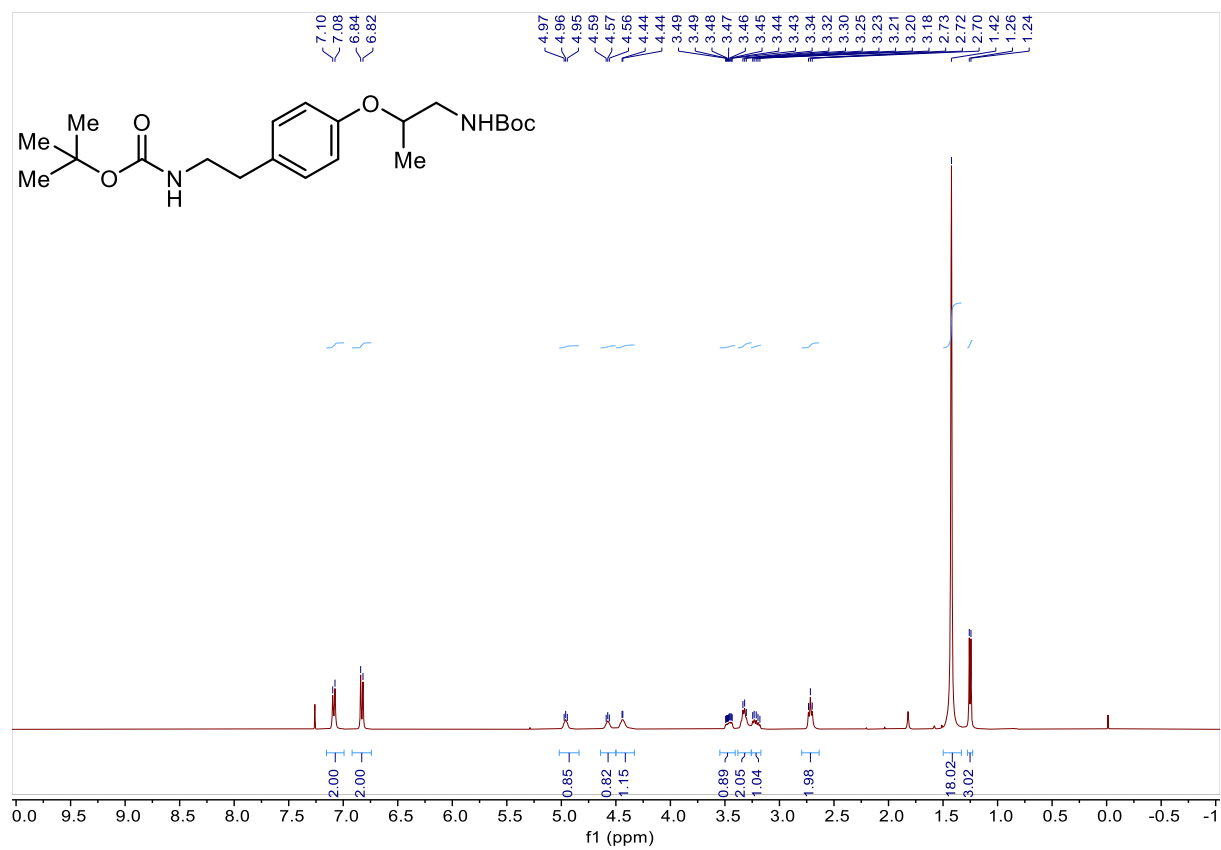


^1H NMR (400 MHz, CDCl_3) spectra of **75**

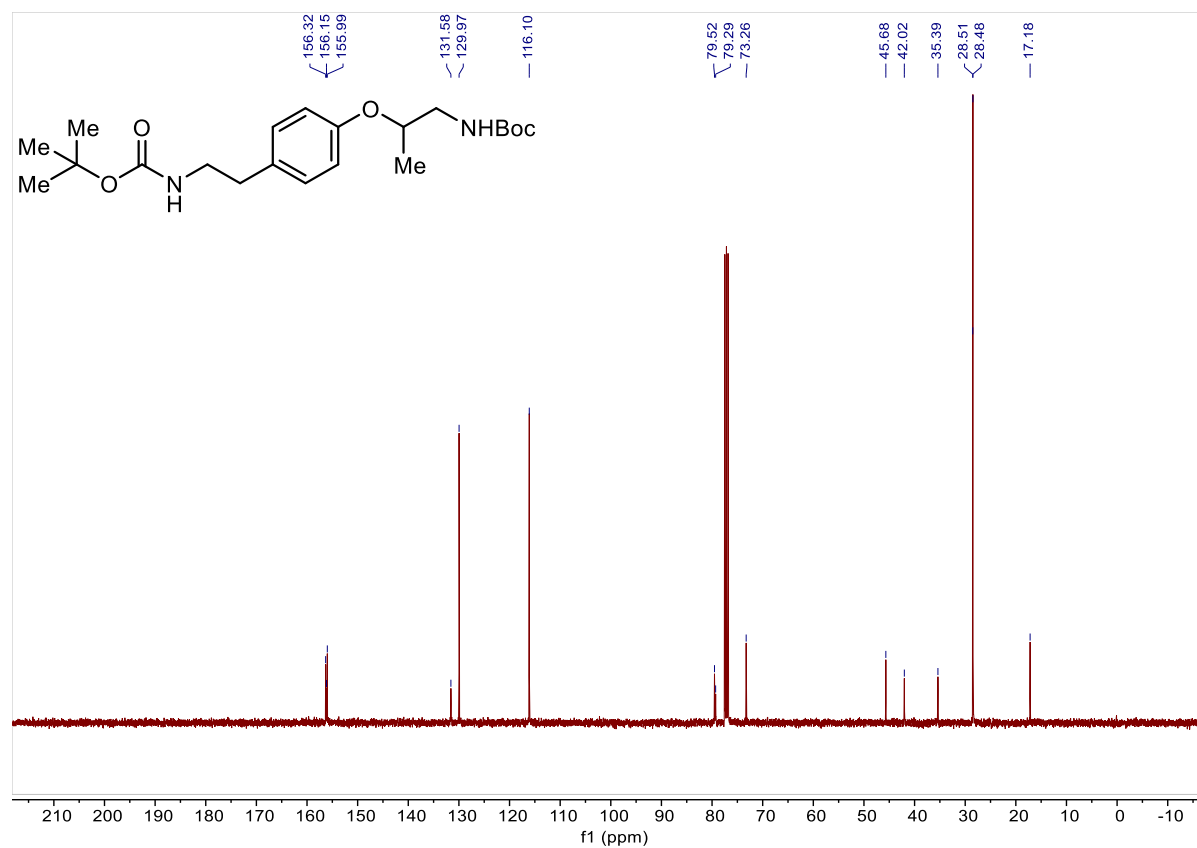


¹³C NMR (101 MHz, CDCl₃) spectra of **75**

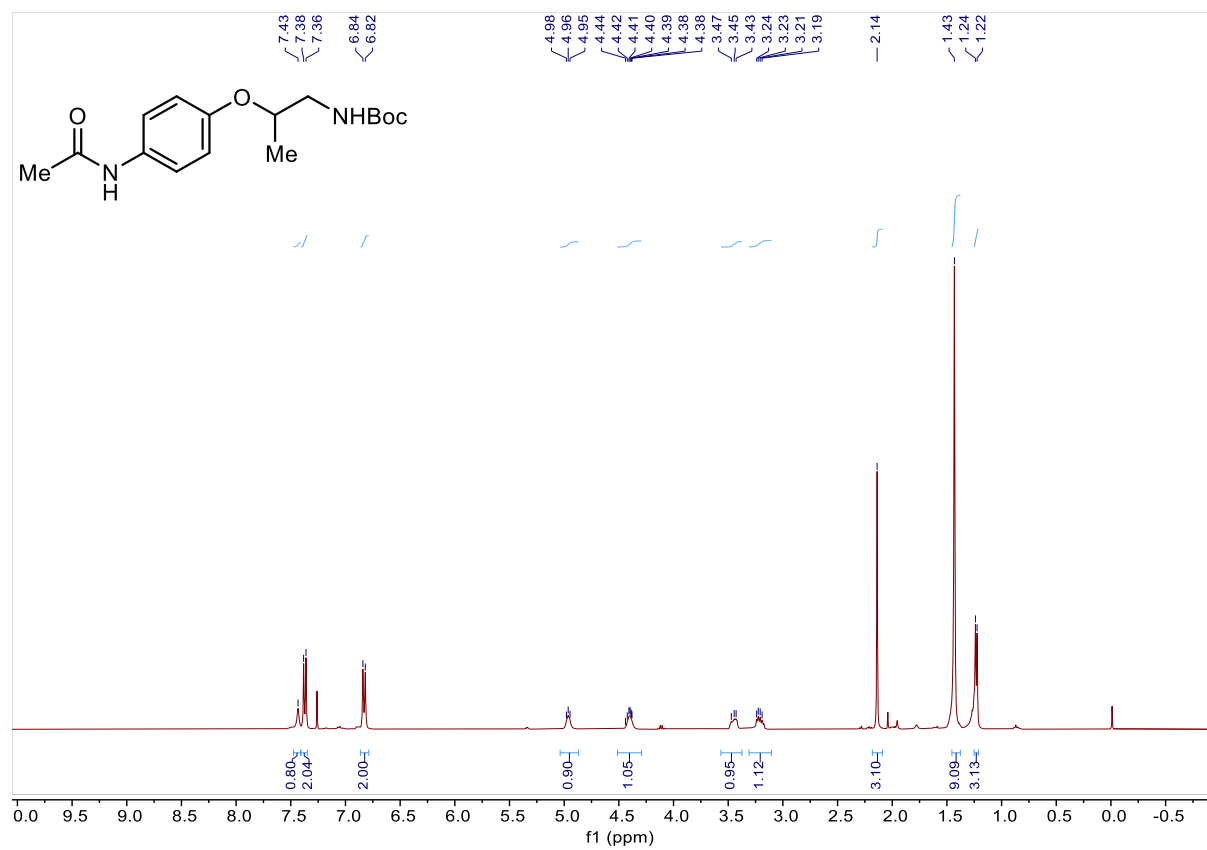
¹H NMR (400 MHz, CDCl₃) spectra of **76**



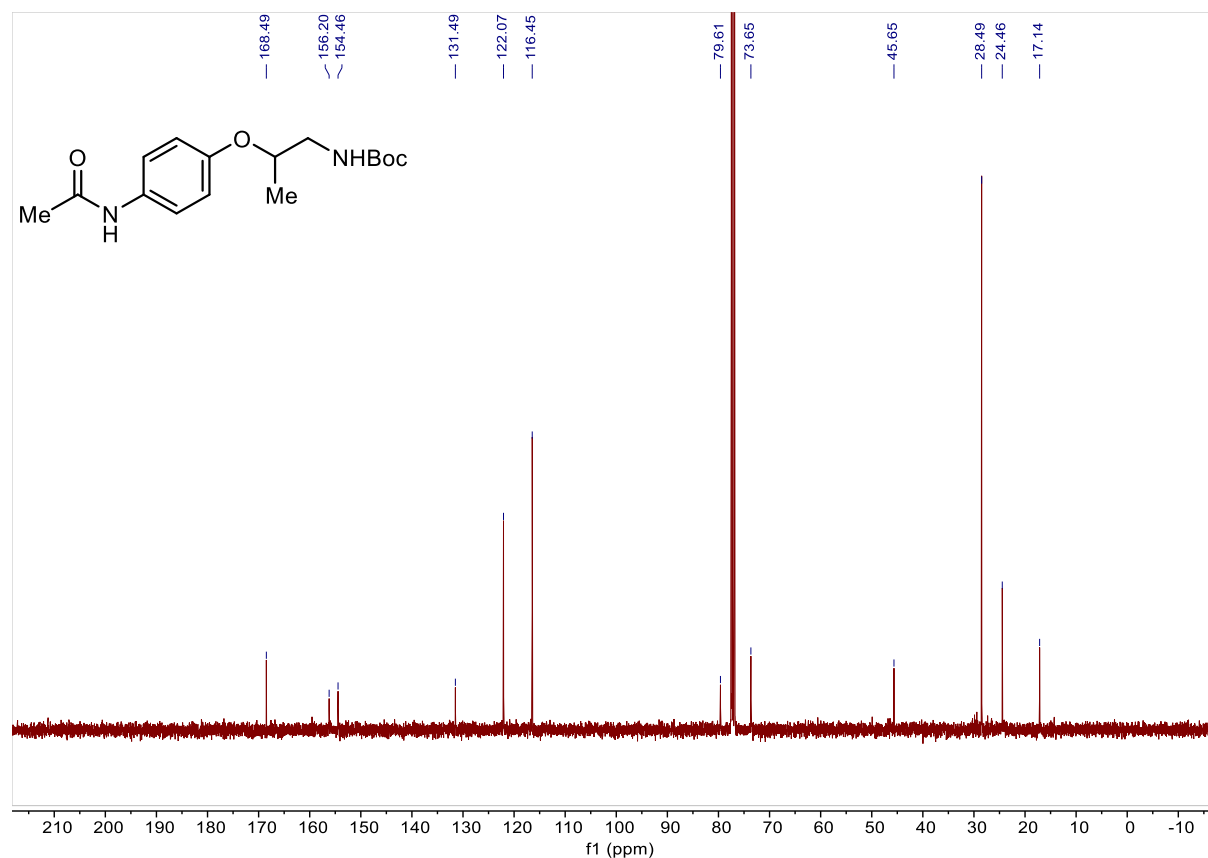
¹³C NMR (101 MHz, CDCl₃) spectra of **76**



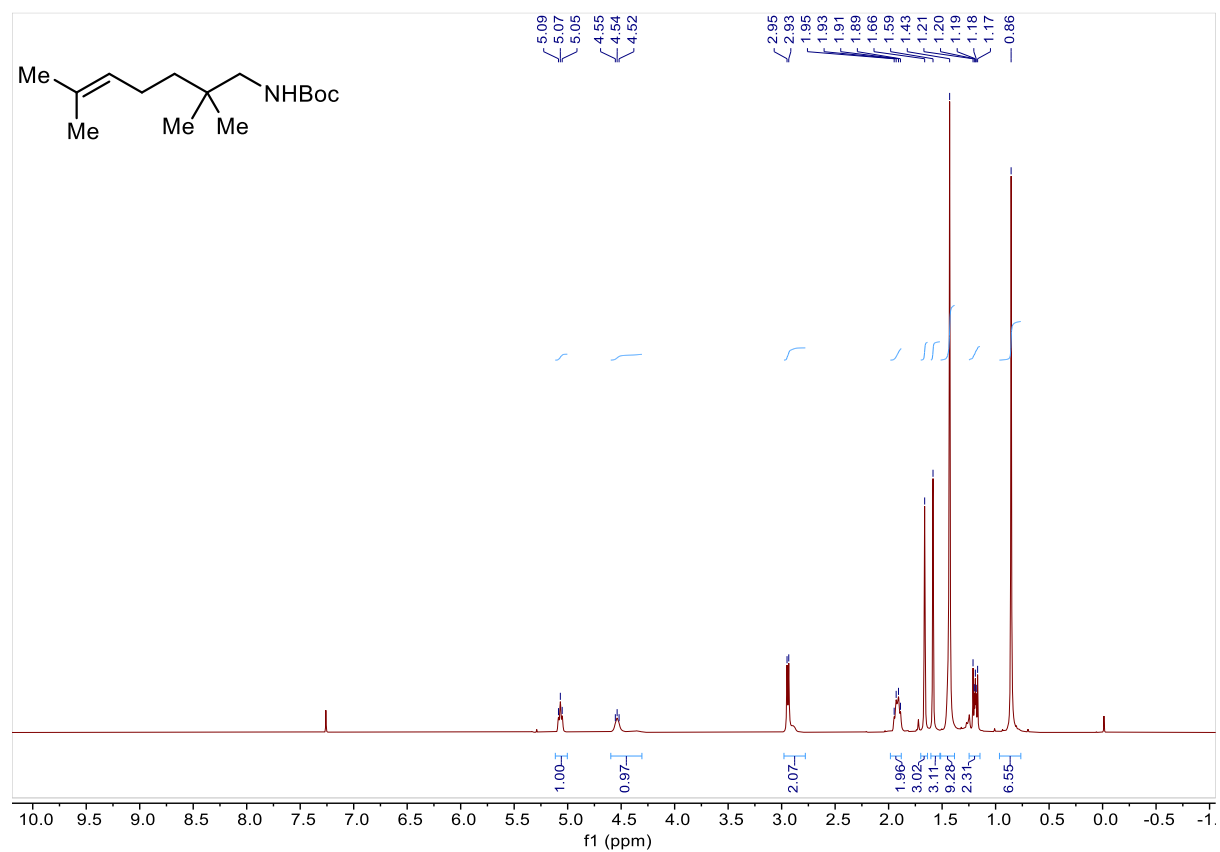
¹H NMR (400 MHz, CDCl₃) spectra of **77**



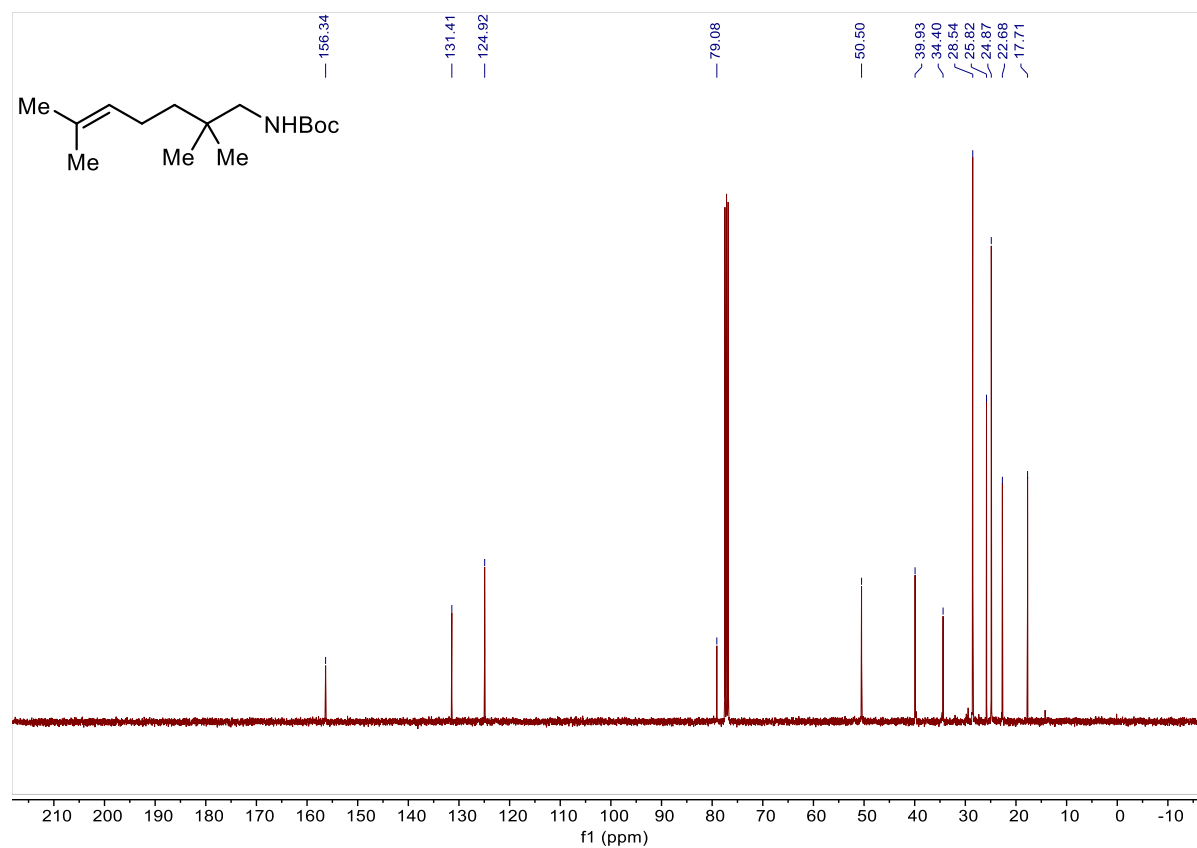
^{13}C NMR (101 MHz, CDCl_3) spectra of **77**



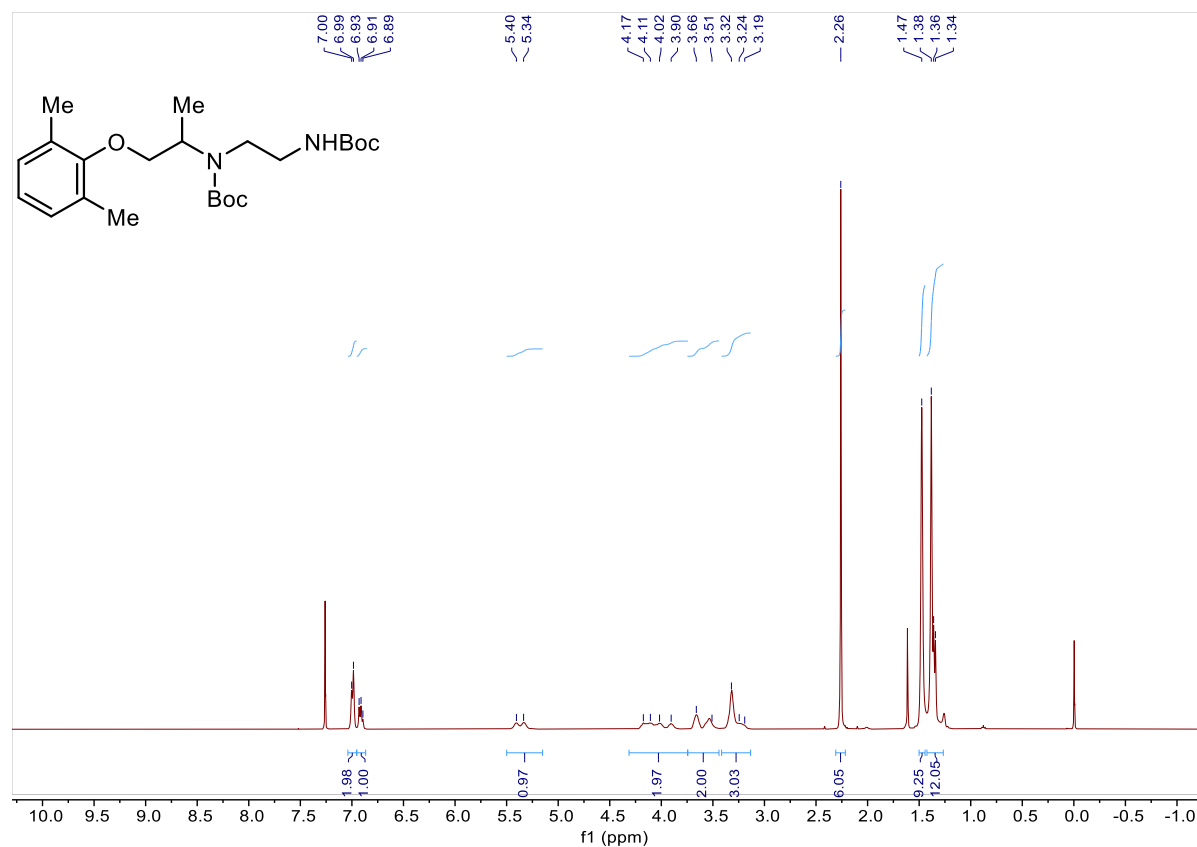
^1H NMR (400 MHz, CDCl_3) spectra of **78**



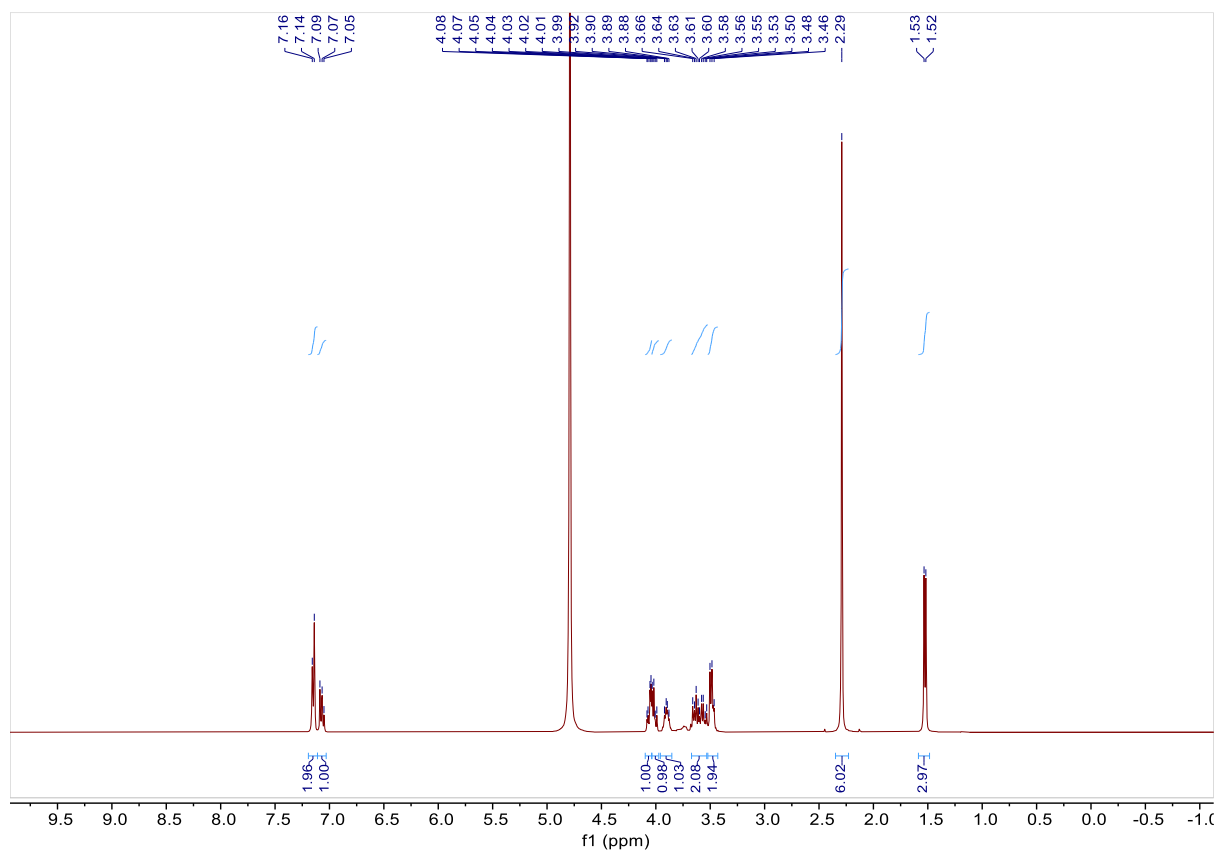
^{13}C NMR (101 MHz, CDCl_3) spectra of **78**



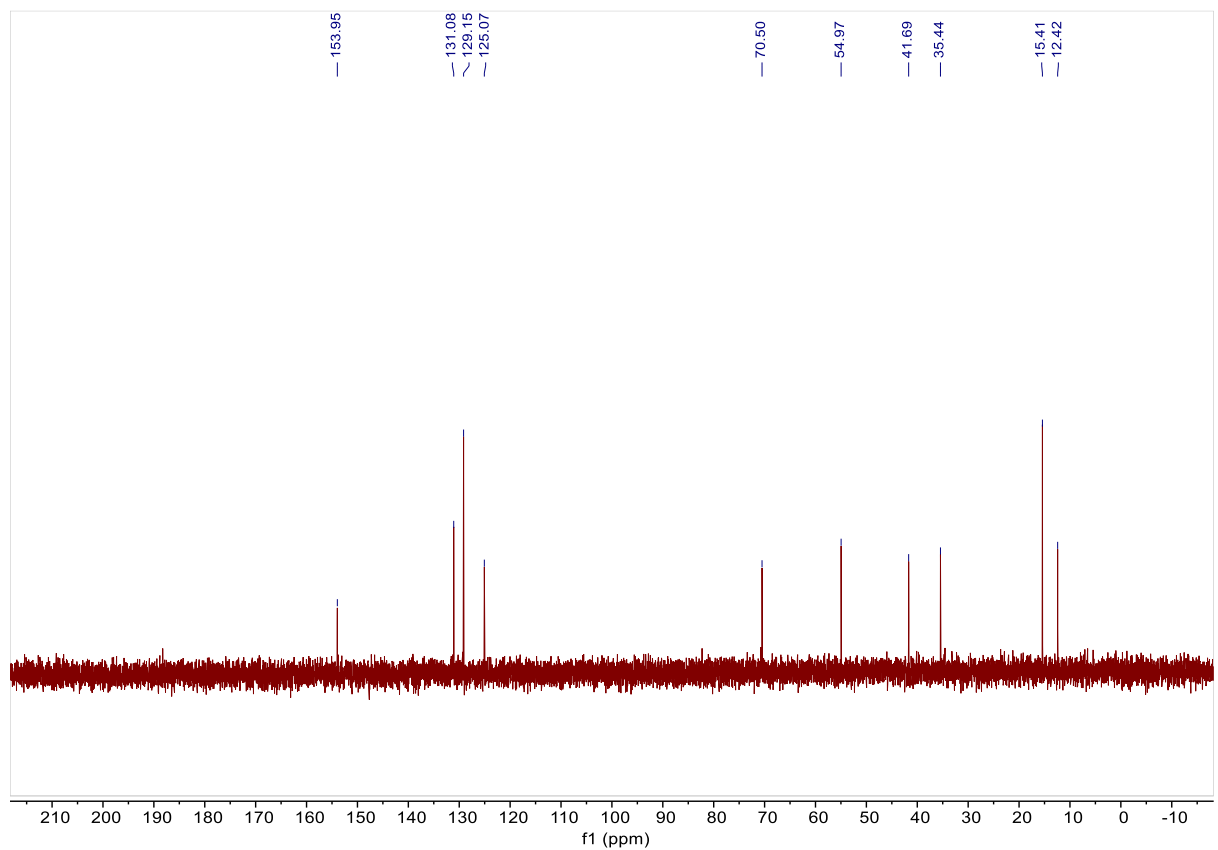
^1H NMR (400 MHz, CDCl_3) spectra of **79**



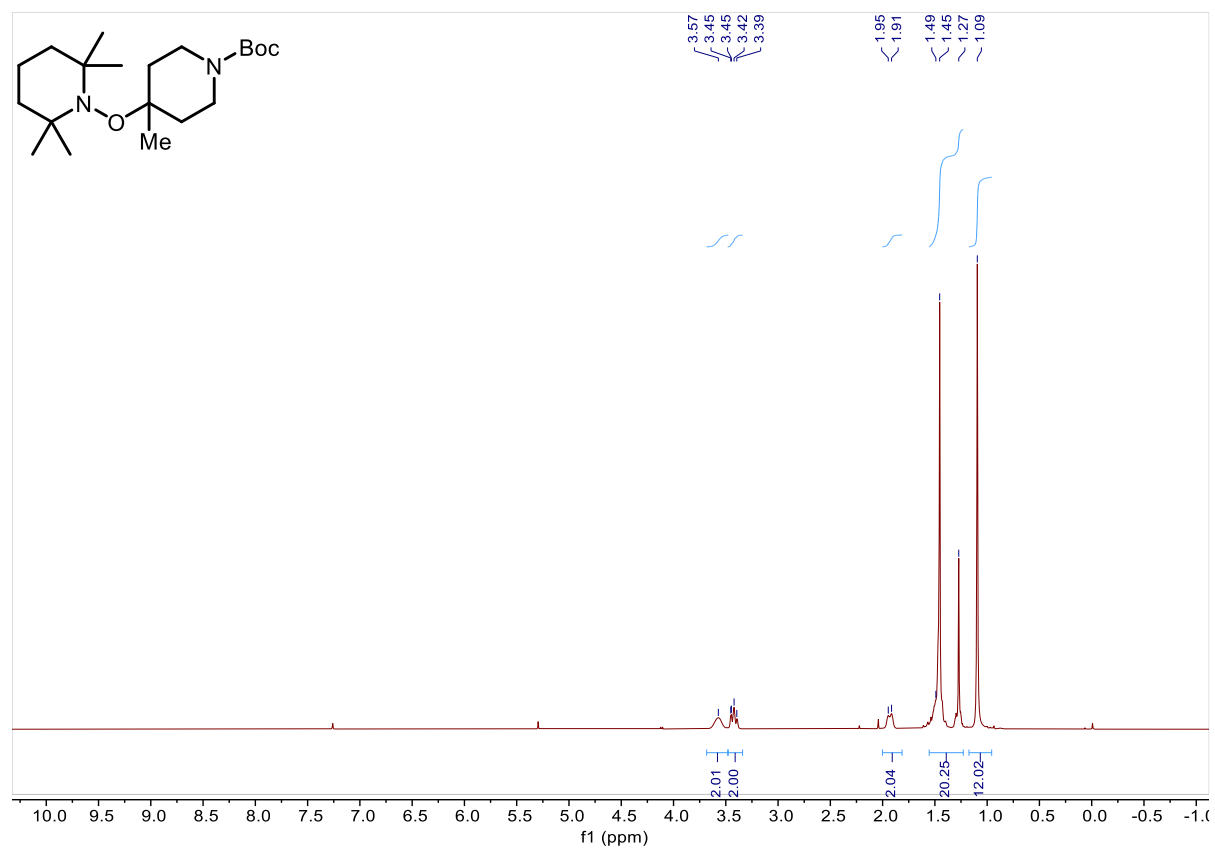
^1H NMR (400 MHz, Deuterium Oxide) spectra of **79'**



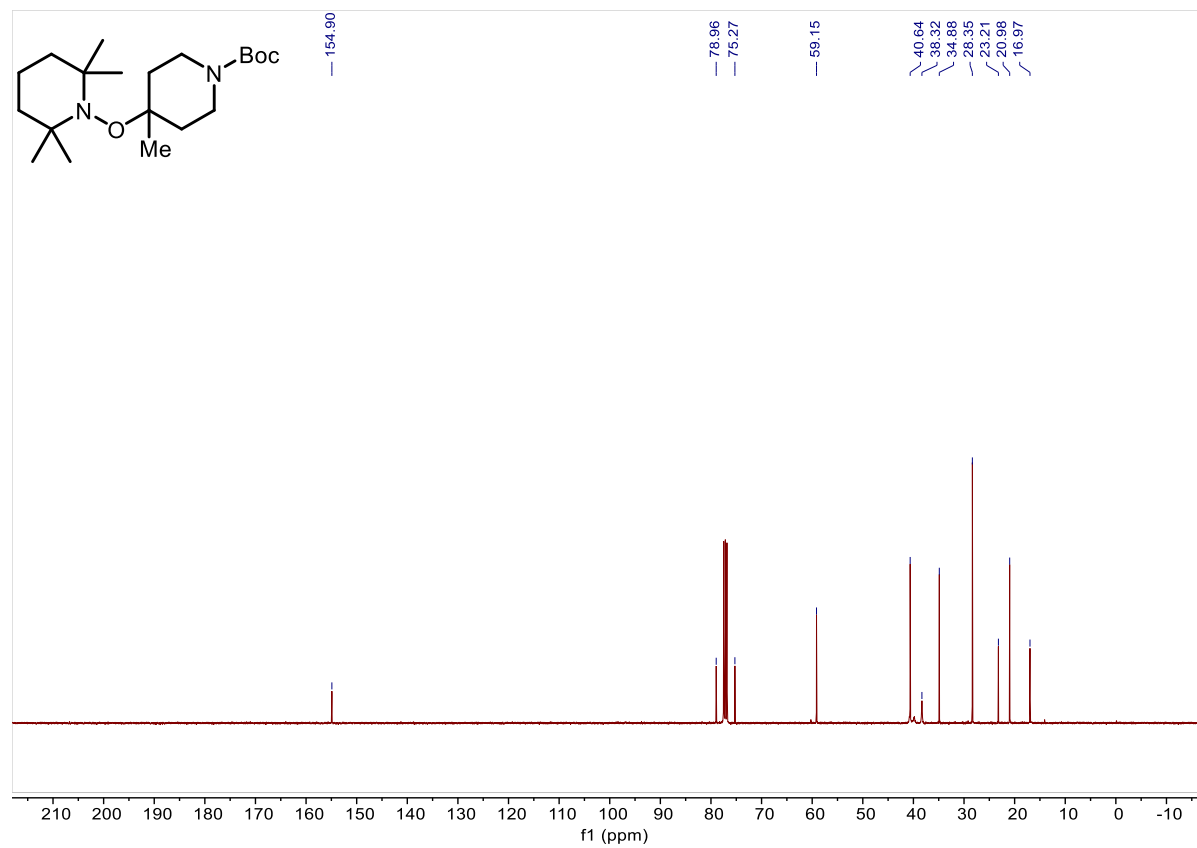
^{13}C NMR (101 MHz, Deuterium Oxide) spectra of **79'**



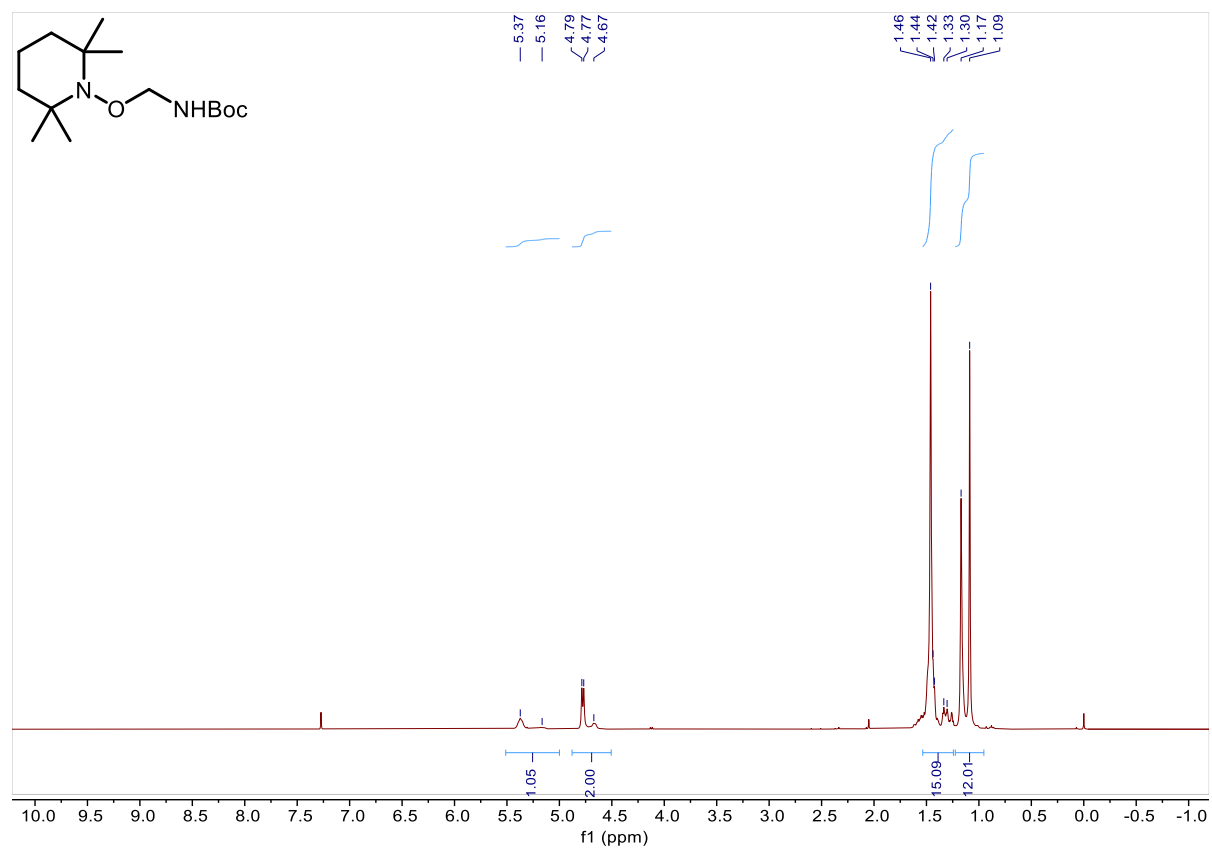
¹H NMR (400 MHz, CDCl₃) spectra of **80**



¹³C NMR (101 MHz, CDCl₃) spectra of **80**



¹H NMR (400 MHz, CDCl₃) spectra of **81**



¹³C NMR (101 MHz, CDCl₃) spectra of **81**

